VOLUME 11 OCTOBER, 1934 NUMBER 4

NATIONAL
RESEARCH COUNCIL
of CANADA

CANADIAN JOURNAL OF RESEARCH

CANADA

Published under the authority
of the
Chairman of the Committee of the
Privy Council on Scientific and Industrial Research

OTTAWA - CANADA

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Publications and Subscriptions

The Canadian Journal of Research is published monthly by the National Research Council of Canada, Ottawa, to which address all correspondence should be directed.

The subscription rate is $3.00 per year to any part of the world. Single copies are thirty-five cents each.

Canadian Journal *of* Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

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RAPID DETERMINATION OF MOISTURE IN GRAIN

II. CALIBRATION AND COMPARISON OF ELECTRICAL MOISTURE METERS WITH VACUUM OVEN FOR HARD RED SPRING WHEAT[1]

BY W. H. COOK[2], J. W. HOPKINS[3] AND W. F. GEDDES[4]

Abstract

The electrical moisture meters studied were: the Burton-Pitt, Davies, Limbrick, hand-operated and motor-operated Tag-Heppenstall. The Burton-Pitt is a "dielectric" type; all the others depend on the resistance principle.

The calibration curve for the Burton-Pitt instrument is parabolic within the range 11.0 to 17.0% moisture. The resistance type instruments all show a linear relation between moisture content and the logarithm of the resistance at moisture contents below 17.0%, and a parabolic relation at higher moisture contents. The accuracy of the meters, as determined by the experimental errors and the standard error of prediction of the vacuum oven moisture, decreases in the following order within the moisture range, 11.0 to 17.0%: motor-operated Tag-Heppenstall, Limbrick, hand-operated Tag-Heppenstall, Burton-Pitt and Davies. At higher moisture contents than 17.0% the Burton-Pitt and Davies instruments are definitely unreliable, and the remaining meters are also less precise.

The temperature coefficient of the wheat-instrument system was found to be appreciably different from that of the wheat alone in the Limbrick and Burton-Pitt. The temperature coefficient was also found to differ somewhat in different moisture ranges. The effect of humidity is most pronounced in the Limbrick, but is in all instruments small in comparison with that of temperature. The limited number of low grade samples studied appeared to follow the same calibration curve as high grade samples in all meters and 28 samples of the hard-kernelled variety Garnet were also found to follow the calibration curve deduced from the general reliability experiments in all meters, with the exception of the hand-operated Tag-Heppenstall. The discrepancy with this meter is not great and can be attributed to the roll space being unsuitable for this hard-kernelled variety.

The moisture range satisfactorily covered by the instruments decreases in the order: motor-operated Tag-Heppenstall, hand-operated Tag-Heppenstall, Limbrick, Burton-Pitt and Davies. In all cases the upper limit is finally determined by the increasing inaccuracy of the meter, rather than by its physical range, which is limited at 21.5% moisture with the Limbrick only when used at the highest sensitivity. With wheat below 11.0% moisture, only the Burton-Pitt and Tag-Heppenstall instruments can be used, and the calibration curve for the Burton-Pitt obtained with wheat of higher moisture content cannot be extrapolated over this lower range.

[1] *Manuscript received September 18, 1934.*

Contribution from the National Research Laboratories, Ottawa, and Dominion Grain Research Laboratory, Winnipeg. Published as paper No. 59 of the Associate Committee on Grain Research.

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1. Introduction

This investigation was undertaken to calibrate and to determine the general utility and accuracy of five electrical moisture testers, namely the Burton-Pitt, Davies, Limbrick and the hand-operated and motor-operated Tag-Heppenstall instruments, when used with hard red spring wheat. The investigation was planned to include a statistical study of the errors of method and observation, sampling error, and daily variations, as already outlined (5) in connection with the results obtained from the same series of wheat samples by the vacuum oven, 130° C. air oven and Brown-Duvel methods.

The meters investigated did not include all the kinds manufactured, the D-K (Schnellwasserbestimmer) and the dielectrometer (moistometer), both well known, being omitted as they were not available at the time this investigation was undertaken. Coleman (4) however, investigated these meters, which operate on a capacity principle, and found them inferior to the Tag-Heppenstall, a resistance type. The dielectric or capacity type was represented in this investigation by the Burton-Pitt. Some preliminary experiments on three of the meters included in the present study have been reported by Birchard (1).

2. Design and Operation of Instruments

Electrical moisture meters may be divided into two general types according to the principle employed. In the so-called "dielectric" type the grain is placed inside the windings of an induction coil or between the plates of a condenser forming part of a high-frequency oscillating circuit. The other type measures the electrical resistance of the grain, using direct current from a battery, and special electrodes.

In the Burton-Pitt dielectric instrument the circuit is so arranged that the direct current component of the plate current is altered by the introduction of the sample, and the accuracy of this class of instrument is therefore dependent on this change being closely related to the moisture content of the material, and on the stability of the oscillating circuit. The work of Burton and Pitt (2) suggests that the results obtained are dependent to some extent on the electrical conductivity, as well as the dielectric properties of the material under test.

The electrical resistance type makes use of the relationship between electrical resistance and moisture content observed in materials which contain soluble salts and relatively small amounts of water. As the electrical resistance of grain is quite high at all ordinary moisture contents, either a sensitive galvanometer, a microammeter, or vacuum tube amplification must be employed for the measurement of the transmitted current. Various types of electrodes are employed in the different makes of instruments and these naturally affect the magnitude of the observed resistances.

Burton-Pitt Tester

Burton and Pitt (3) describe the Burton-Pitt tester and give the results obtained from a series of determinations. In these the wheat was placed in a standard test tube, without weighing, and the tube inserted in the induction coils of the instrument. In the instrument provided for the present investigation, however, the grain is placed between the plates of a condenser, contained in a test cell connected to the instrument by means of flexible cord, an arrangement they presumably found to give more satisfactory results. The instrument as originally received was fitted with a 201A vacuum tube, but on the recommendation of Prof. Burton this was replaced by a 112A tube which was found to give more consistent readings. The sensitivity employed in these tests was a milliammeter deflection of 90 when the constant capacity condenser was in the circuit. The setting of the zero point and the sensitivity were checked before each test and minor adjustments were frequently found necessary.

After making the above adjustments with the empty test box connected to the instrument, the actual test consisted merely of weighing out the desired amount of grain, pouring it into the test box and reading the milliammeter. As the instrument settings are sometimes altered slightly by moving the cell, such movements should be avoided. For the purpose of the present tests the cell was mounted in a wooden block having a wooden slide which fitted flush with the bottom; drawing this slide discharged the grain after the test. The cell held 100 gm. of wheat of relatively low bushel weight, so this quantity, weighed to within ± 0.1 gm. was employed in the test. The wheat was poured in uniformly without packing.

This meter can hardly be regarded as a readily portable instrument, for although the meter unit proper is not large, the battery box, containing a storage cell and rectifier in addition to the dry batteries, is large and heavy. Moreover, if the instrument is to be used for making any number of tests it must be operated near a source of electric current in order to charge the storage cell. About 6 sq. ft. of table space is required for operation in addition to a smaller space beneath the table to accommodate the batteries. The only accessory equipment required is a balance for weighing the grain. The time required to make a test is discussed, in relation to the other meters, toward the end of this section but it should be noted that the instrument must be connected up from 20 to 30 minutes before it is to be used in order to allow the tube to warm up and become stable.

Davies Moisture Meter

The Davies moisture meter operates on the resistance principle and has been described by the inventor (6). It was the simplest instrument of this type tested, consisting only of a test-cell, sensitive galvanometer, standardizing and protecting resistances, switch, and battery, all of which are contained in a compact carrying case. The protecting resistance is permanently in series with the galvanometer, and when the switch is turned to the standard-

izing position the galvanometer deflection gives a measure of the battery voltage, which is adjustable in increments by means of wander-plugs fitting into holes in the battery.

In preliminary work it was found that the instrument was not sufficiently sensitive to give a deflection of measurable magnitude with "straight" grains. As the galvanometer gave a full scale deflection at 46.86 volts, a voltmeter of high resistance was connected to the instrument, and readings taken at 100 volts on all samples giving small deflections at 46.86 volts. A further modification consisted of placing a 10,000-ohm potentiometer in the battery circuit so that the voltage could be varied continuously, it having been found that adjustments by means of the wander-plugs could not be made closely enough for accurate work. Preliminary tests were made using both ground and whole wheat, as the instructions did not state which was to be used. The ground samples gave somewhat greater deflections but this increase in sensitivity was not sufficient to give significantly higher readings with dry grain. The actual tests of this instrument were therefore made with whole wheat.

The Davies meter was the smallest and most readily portable instrument of those tested, and required only about 2 sq. ft. of space for its operation. The instrument is entirely self-contained and no preliminary grinding or weighing of the sample is necessary. The grain, however, must be packed in the test cell by hand, using a heavy plunger. The electrodes are placed in the bottom and on the sides of the test cell, and it is asserted that the reading is independent of the amount of grain, provided the depth of the sample, after packing, exceeds 3 cm. Although Davies (6) has shown that some form of polarization occurs in these test cells he feels that this does not vitiate the method as long as a constant voltage is used for calibration and testing. No attempt was made to study the effect of polarization in this investigation, but the experiments were arranged so that a sufficient number of samples would be tested at each voltage employed to provide a reliable calibration curve.

Limbrick Moisture Tester

The Limbrick moisture tester (8) also operates on the resistance principle, the resistance of the sample being compared with a resistance bank which is adjustable by increments. Vacuum tube amplification is employed in conjunction with a milliammeter for measuring the current. In order to overcome any error arising from aging or other change in the vacuum tube, the deflection of the milliammeter is observed while a push button which places the grain only in the circuit is depressed. Another push button is then depressed which places the resistance bank only in the circuit and the resistance is then adjusted to give the same deflection as the grain. Adjustments are provided for setting the meter at the desired sensitivity. The instrument studied was the 20A, the larger and more accurate of the two models made.

Before a test can be made, the grain must be ground in a small hand mill supplied with the instrument. The burrs in this mill are set to grind the

grain rather coarsely, adjustment being made at the factory. The grain is not weighed, but a constant volume of the ground material is measured out in a measuring cup and introduced into the test cell through a small hopper. The meter unit proper is somewhat larger and heavier than the Davies, but apart from the grinder, it is self-contained. Only a few minutes are required for the amplifying tube to warm up before a test can be made. Ordinarily this instrument, including the grinder, requires about 4 sq. ft. of table space.

Tag-Heppenstall Meters

The hand-operated Tag-Heppenstall moisture meter has already been described by Coleman (4) and by Geddes and Winkler (7). Both hand- and motor-operated models consist of two distinct parts, the roller electrodes and the meter unit for measuring the current. The latter consists of an Ayrton shunt, a sensitive microammeter, batteries, and a resistance for adjusting the current. The electrodes consist of two corrugated rollers. Although the meter unit is the same for both hand- and motor-operated electrodes, the electrodes themselves differ considerably, those of the motor-operated model being much larger. The hand-operated model is easily portable, the roller electrodes being somewhat heavier than the Limbrick grinder, but the instrument itself less bulky. No external source of electric current is required. The electrodes of the motor-operated model are much heavier and as current is required to operate the motor this can scarcely be regarded as a thoroughly portable instrument. The hand model requires about 4 sq. ft. of table space and the motor model slightly more.

The roller electrodes appear to be superior to the test cells with static electrodes used in the other resistance-type instruments. They are rapid in operation (see Table I), and no grinding, weighing or measurement is required. Although no attempt was made to determine the extent to which polarization affects the results obtained with the different meters, it seems likely that this effect had the least influence in the Tag-Heppenstall meters, since both the electrodes and sample are in continuous motion throughout the test. Another advantage of the roller electrodes is that impurities in the grain, such as a piece of metal, will cause the needle to jump but will not affect the "average" reading obtained, whereas in test cells such foreign matter will undoubtedly affect the resistance, and consequently the apparent moisture content. The observed resistances with the roller electrodes are also much lower than those to be measured in the test cells of the Limbrick and Davies meters.

Time of Operation

Although these instruments are all classed as rapid testers, there was a considerable difference in the time required to operate the different makes. The average time required for making duplicate tests, by the two operators allotted at random to the instruments during the general reliability test, was noted and is recorded in Table I. The reported times cover only the actual period required for manipulating the instrument and accessories

(grinder and balance where required) and do not include the time consumed in selecting samples, making interpolations, or reading conversion charts, etc. The motor-operated Tag-Heppenstall was found to be the most rapid of the testers investigated, while the hand-operated model was only slightly slower. Although frequent adjustments are necessary in operating the Burton-Pitt the actual operation of the meter is usually not as time-consuming as the preliminary weighing of the sample. The Davies instrument was found to be relatively slow. The sensitivity had to be changed frequently, and as the galvanometer pointer was not damped properly, some time was required for it to come to rest. The Limbrick was the slowest, partly because the grain had to be ground but chiefly because the manufacturer's instructions required three independent grindings and readings to be taken on each sample. According to these instructions the first of these readings is not to be used, since it might be in error due to moisture remaining in the cell from the previous sample, etc. In order to determine whether or not this first reading is less reliable than the other two, the deviations of the first trial from the means of Trials 2 and 3 were compared with the variance of Trials 2 and 3 individually. This was done on 120 samples distributed throughout the entire moisture range, and there was no significant difference in these variances, suggesting that the first reading need not be considered less trustworthy than the other two. The time of operation, as given in Table I, can therefore be reduced to about two-thirds of the reported value, or 3.6 min. for a duplicate test. Even so, this meter is still one of the slowest in operation.

TABLE I

RAPIDITY OF DETERMINATION OF MOISTURE BY ELECTRICAL METERS

Meter	Average time for duplicate determinations (min.)
Tag-Heppenstall (motor)	1.2
Tag-Heppenstall (hand)	1.5
Burton-Pitt	2.4
Davies	3.7
Limbrick	5.4

3. Experimental Details

All the instruments were operated in accordance with the instructions supplied by the manufacturers, and with minor exceptions no effort was made to determine the best technique, operating conditions, or settings employed. The instruments were examined and tested thoroughly in the Physics Division of the National Research Laboratories before and after the investigation to insure that none was defective during the tests. The resistances corresponding to different meter readings, for all instruments operating on the resistance principle, were determined prior to the actual tests, so that the moisture values could be plotted as a function of the resistance in making the calibration charts. It was felt that a calibration chart showing the relationship between resistance and moisture content would be of more general utility than one showing the moisture content at various meter readings, since the latter would be applicable only to particular instruments. To adjust the

resistances on each instrument accurately would be more difficult than measuring the actual value. If this value is known the data obtained in this investigation should be applicable to the calibration of any instrument of a particular make, provided the test cell is of the same construction and dimensions throughout.

In the general reliability tests, two operators read the five meters. To avoid any systematic error due to personal factors, a separate random allotment of meters and operators was made for each sample. In determining the temperature and humidity coefficients, one operator read all the instruments. Before any of the tests were undertaken the operators, who were skilled laboratory technicians, were trained for several days in the use of all the instruments.

It was planned originally to make all of the meter tests in a room maintained at a constant temperature of 72° F. and a constant relative humidity of 40%. Owing to the number of men in the room however, the temperature frequently rose to 75° F., with the result that it was necessary to apply temperature corrections to the majority of the observed instrumental readings. These changes in temperature also caused some fluctuation in the relative humidity, but it will be shown later that these small variations had no significant effect on the results. In the experiments on the effect of temperature and humidity only one man worked in the room, and the required conditions were maintained within $\pm\frac{1}{2}$° F. and $\pm 2\%$ relative humidity.

The temperature of the grain was measured in all experiments, and since all samples had been stored in the testing room for 24–36 hr. their temperature seldom differed from that of the room and instrument by more than $\frac{1}{2}$° F. When such differences occurred, the temperature of the grain was employed in making subsequent calculations. As only one of the meters, the Limbrick, is provided with a thermometer in the test cell, the temperature of the grain used in the other instruments was determined just before it was tested. Since the temperature of the room and the grain were practically the same, only 30–60 sec. were allowed for the thermometer to reach equilibrium before the temperature reading was taken. Grinding the grain for the Limbrick usually raised its temperature 2–3° F. above that of the room, and in this case the temperature was read 30 sec. after placing the grain in the cell, as recommended by the manufacturer.

As previously described (5, § 2) the wheat samples employed were allowed to stand for one month in moisture-tight cans before testing. Under these circumstances a reasonably uniform distribution of moisture throughout the entire sample is to be expected. Grain freshly sampled from a car or bin may, however, be more heterogeneous, in which case, as suggested by Birchard (1, p. 16), less accurate results may be obtained.

4. Effect of Temperature

It is well known that the electrical resistance of any substance varies with the temperature, and in consequence the reading obtained from an instrument

of the resistance type will depend on the temperature at which the test is made as well as on the moisture content of the grain. Coleman (4) has shown that the temperature coefficient of grain is so high that fluctuations of even a few degrees will affect the results appreciably. An accurate knowledge of the temperature coefficient is therefore essential if precise results are to be obtained. There appears to be some diversity of opinion as to whether temperature corrections are necessary with the dielectric type of meter. Burton and Pitt (3) state that the readings obtained with their instrument are independent of the temperature and humidity of the room in which it is used. *A priori*, a temperature effect is to be expected regardless of whether the quantity observed is dependent on the dielectric constant of water or the conductivity of the material, since both of these properties are known to be affected by temperature. Coleman has pointed out that instruments of the dielectric type do not give the same readings with grain of different temperatures, and that the temperature coefficient of the dielectric constant of water does not account for the whole of the observed effect; he suggests also that the temperature coefficient of these instruments may not be linear through a range of moisture content.

In commercial testing two kinds of temperature variation may arise. The instrument and grain to be tested may be at the same temperature, *i.e.*, the temperature of the test room, in which case the temperature effect will depend on the combined temperature coefficient of the grain-instrument system; or the grain, freshly collected from a car or bin, may have a much higher or lower temperature than that of the instrument, the additional effect in this case depending on the temperature coefficient of the grain only.

These two temperature coefficients, and the humidity coefficient, were determined for thirty samples of wheat of different grade and moisture content, as shown in Table II; no artificially dampened samples were employed. Each sample was cleaned and subdivided into 56 subsamples using the riffle sampler and method previously described (5). These were allotted to the different instruments and conditions of test at random, five sets of subsamples being used for the vacuum oven determination. The results obtained by this method appear in the table, and the variations observed between different trials are doubtless, judging from the work already reported, due chiefly to sampling errors. It was found during the reliability tests, to be described later, that the Davies meter was of little value for estimating the moisture content of wheat, and therefore no data were obtained regarding the effect of temperature and humidity on the readings of this meter.

In determining the temperature coefficient of the wheat only, the instruments were kept at a temperature of 72° F. $\pm \frac{1}{2}$° F. and a relative humidity of 30% $\pm$ 2%, and the grain was adjusted to temperatures of 0° F., 32° F., 72° F. and 100° F., by means of a thermostat where necessary. This wide temperature range was employed partly because it was felt that under certain climatic conditions such extremes in grain temperature might occasionally be

TABLE II

GRADE AND VACUUM OVEN MOISTURE CONTENT OF WHEAT SAMPLES USED IN STUDYING EFFECT OF TEMPERATURE AND HUMIDITY ON MOISTURE METER RESULTS

Sample No.	Grade	Percentage moisture by vacuum oven					
		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average
WS1-E	1 Northern	12.28	12.30	12.28	12.30	12.24	12.28
WSH-2A	1 Hard	13.16	13.10	13.08	13.10	13.04	13.10
WS1-D	1 Northern	13.16	13.16	13.10	13.06	13.12	13.12
WS1-C	1 Northern	13.50	13.50	13.52	13.50	13.54	13.53
WS1-B	1 Northern	13.94	14.08	14.01	14.02	13.94	14.00
WS2-A	2 Northern	14.68	14.69	14.58	14.54	14.58	14.61
WS2-B	2 Northern	14.20	14.34	14.30	14.30	14.28	14.28
WS2-C	2 Northern	14.38	14.36	14.32	14.20	14.34	14.32
WS1-A	1 Northern	14.48	14.52	14.46	14.26	14.44	14.43
WS2-D	2 Northern	15.48	15.58	15.57	15.53	15.58	15.55
WT1-A	Tough 1 Nor.	14.60	14.46	14.74	14.62	14.74	14.63
WT2-B	Tough 2 Nor.	15.39	15.48	15.41	15.34	15.37	15.40
WT4-A	Tough 4 Nor.	15.26	15.32	15.32	15.28	15.32	15.30
WT2-C	Tough 2 Nor.	15.64	15.66	15.72	15.46	15.78	15.65
WT5-B	Tough 5	15.53	15.50	15.56	15.37	15.50	15.49
WT2-D	Tough 2 Nor.	—	15.56	15.63	15.42	15.70	15.58
WT4-B	Tough 4 Nor.	15.80	15.82	15.92	15.77	15.98	15.86
WT4-C	Tough 4 Nor.	16.54	16.54	16.40	16.38	16.50	16.47
WT5-A	Tough 5	16.04	16.23	16.38	16.24	16.26	16.23
WT3-A	Tough 3 Nor.	16.57	16.70	16.86	16.50	16.40	16.61
WD4-F	Damp 4 Nor.	17.00	16.98	16.86	16.69	16.82	16.87
WDF-A	Damp Feed	17.51	17.56	17.58	17.61	17.66	17.58
WD6-C	Damp 6	18.77	18.77	18.68	18.61	18.69	18.70
WD3-C	Damp 3 Nor.	19.56	19.38	19.64	19.30	19.45	19.47
WD4-E	Damp 4 Nor.	19.16	19.14	19.08	18.95	19.00	19.07
WD2-A	Damp 2 Nor.	19.35	19.45	19.32	19.54	19.39	19.41
WD5-A	Damp 5	20.25	20.52	20.52	20.49	20.60	20.48
WD3-B	Damp 3 Nor.	21.70	21.68	21.44	21.78	21.78	21.68
WD4-A	Damp 4 Nor.	19.03	18.87	18.94	18.96	18.98	18.96
WD4-D	Damp 4 Nor.	21.09	21.04	20.88	21.00	20.99	21.00

experienced, and partly because it seemed desirable to obtain qualitative information as to whether the temperature effect was linear over this wide range. The hand-operated Tag-Heppenstall instrument was not included in this experiment.

It was found impossible to maintain the grain at exactly the above temperatures, even with the precaution of wrapping the cans, as removed from the thermostat, in a heavy towel. The actual temperature of the grain at the time of making the test was therefore determined. Some difficulty was experienced here as a considerable period is required for a thermometer to reach equilibrium in such material. The practice was finally adopted of transferring the thermometer rapidly from one sample to the next and allowing it to come to equilibrium in the latter while the former was being tested. The greatest source of error, however, arose from the fact that cold grain tended to cool the electrodes and test cells, and *vice versa*. In consequence the meter readings on any one sample showed a drift with time, and a similar effect may also have operated from sample to sample since the first ones tested tended to cool or warm the electrodes and decrease the temperature

differential in subsequent tests. The effect of the temperature drift observed in the individual samples was eliminated as far as possible by taking a meter reading as soon as it was practicable after the grain was introduced. As a second reading taken later was invariably different, only the first was employed in the graphs and calculations. The extent to which the cooling of the electrodes by one sample affected the reading obtained on the next sample could not be definitely determined, and although it seems probable that this effect was small, the experiment as a whole cannot be considered as of great precision.

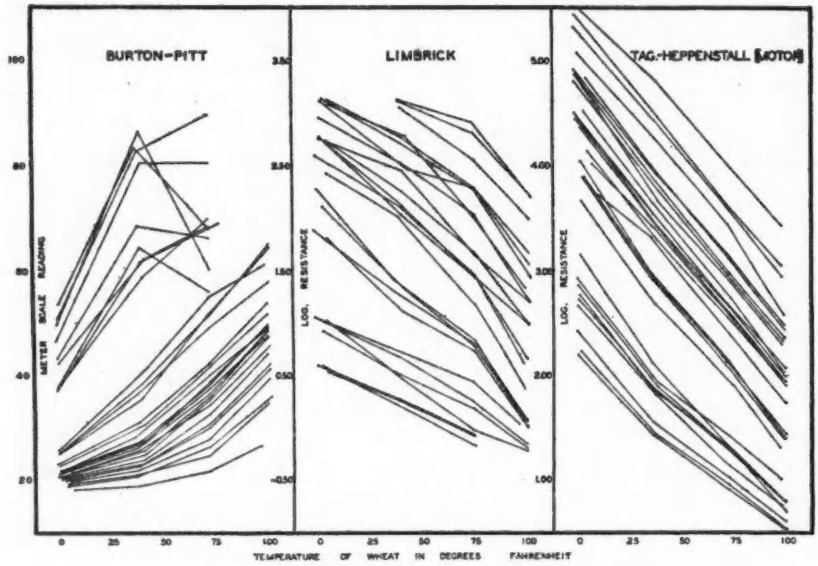

FIG. 1. *Effect of temperature of wheat on meter reading.*

The results obtained are shown in Fig. 1, in which the readings and logarithms of the resistance obtained at different temperatures in the Burton-Pitt and resistance instruments respectively, are plotted against the temperature. Readings obtained on the Burton-Pitt instrument are exceedingly erratic when the deflection exceeds 50 scale divisions. With this instrument the relation between temperature and meter readings appears to be curvilinear with samples of low moisture content, the curve tending to become straighter with greater slope as the moisture content increases.

Since the resistance of grain decreases with temperature the resistance type instruments have a positive coefficient in terms of moisture. The logarithm of the resistance, rather than the resistance itself, is employed as the former was found to be more directly proportional to the moisture content. Owing to differences in design, the resistances to be measured in the Limbrick are much greater than those encountered in the Tag-Heppenstall instruments. In the former case, therefore, the megohm, and in the latter

1,000 ohms, were selected as the units of resistance. It is difficult to say whether the temperature effect with the Limbrick is linear or curvilinear, but owing to the evident irregularity only a straight line was fitted to the points. The motor-operated Tag-Heppenstall results indicate that for the most part the temperature coefficient is linear throughout the temperature range studied.

The approximate temperature coefficient of each sample was determined graphically, the average values for the straight, tough, and damp classes being shown in Table III. It is evident that the temperature coefficient of wheat in the Burton-Pitt instrument is positive and also that it increases with the moisture content for straight and tough grain. The results obtained with damp wheat were erratic and the form of the curves in Fig. 1 suggests that different coefficients are applicable to different temperature ranges. The temperature coefficient in the resistance instruments, in terms of resistance, is negative and appears to be greatest at the intermediate resistances, *i.e.*, with tough grain. The magnitude of the difference between the three moisture classes is greater with the Limbrick than with the Tag-Heppenstall meter. The interpretation of these coefficients will be deferred until the moisture content–resistance relationships have been established in a later section of this paper.

TABLE III

TEMPERATURE COEFFICIENT OF WHEAT IN MOISTURE METERS (METERS AT CONSTANT TEMPERATURE)

Meter	Temperature coefficient per ° F.			Unit of measurement
	Straight*	Tough*	Damp*	
Burton-Pitt	0.21	0.31	0.72[1]; −0.10[2]	Meter scale division
Limbrick	−0.0160	−0.0203	−0.0121	Logarithm of resistance in megohms
Tag-Heppenstall (motor)	−0.0241	−0.0244	−0.0200	Logarithm of resistance in 1000's of ohms

**For exact definition of moisture limits see Table I, previous paper (5).*
[1] *0–32° F.* [2] *32–72° F.*

The determination of the temperature coefficient of the grain–instrument system was effected with greater precision owing to the elimination of the error arising from differential temperature conditions. Further subsamples of the thirty samples referred to were employed for this purpose. A series of six temperatures covering the range ordinarily experienced in a room, namely, 60, 66, 72, 78, 84, and 90° F., was employed. The actual temperature seldom varied more than $\pm\frac{1}{2}$° F. from the desired value, and where there was a slight variation between the temperature of the grain and the room, the temperature of the grain was used in subsequent calculations. The relative humidity was maintained at 30% ± 2% at all the temperatures employed in this experiment. It was recognized that this constant relative humidity did not represent the

same vapor tension, but it was felt that a fixed relative humidity at the different temperatures was a better approximation of the conditions obtaining in practice than either a fixed absolute humidity or a fixed vapor tension deficit.

The results obtained are plotted in Fig. 2. For the most part the ordinary deviations from a linear relationship between meter reading and temperature can be attributed to sampling and experimental errors. The Burton-Pitt, however, gave erratic results with nearly all of the samples containing sufficient moisture to result in deflections exceeding 50 to 60 scale divisions, and it appears therefore that this is due to some inherent fault in the instrument. There are two points that are seriously out of line in the motor-operated Tag-Heppenstall chart, but these are believed to be due to some mistake on the part of the operator.

Examination of Fig. 2 suggests that the temperature coefficient varies with the moisture content of the grain. In order to determine the temperature coefficient, a straight line was fitted to the points obtained with each

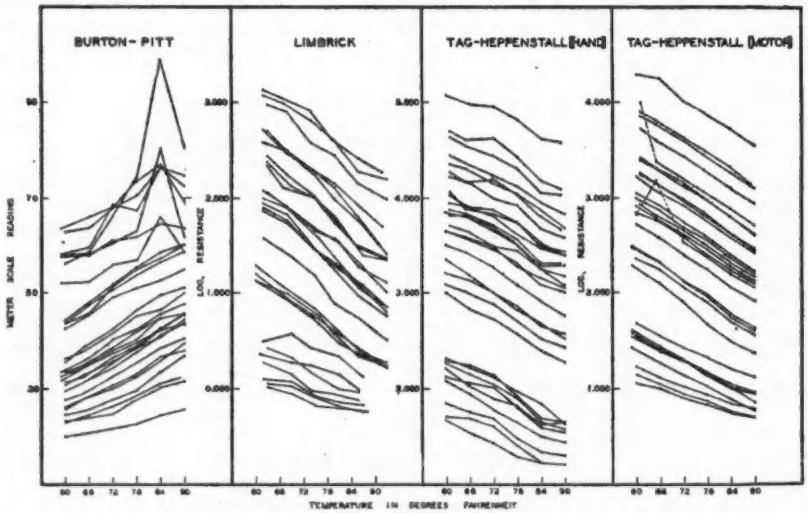

FIG. 2. *Effect of temperature of wheat—instrument system on meter reading.*

sample by the method of Least Squares. Since the high moisture samples gave erratic results in the Burton-Pitt, especially at temperatures above 78° F., the straight line was fitted only at intermediate temperatures in the neighborhood of 72° F. In Fig. 3, the slope of the line, representing the temperature coefficient, is shown plotted against the meter reading or logarithm of the resistance of the sample at 72° F. which is proportional to the moisture content. As the temperature of the grain tested in the Limbrick instrument was always increased by grinding, these results are computed to a basis of 75° F. It is evident from the figure that the temperature coefficient

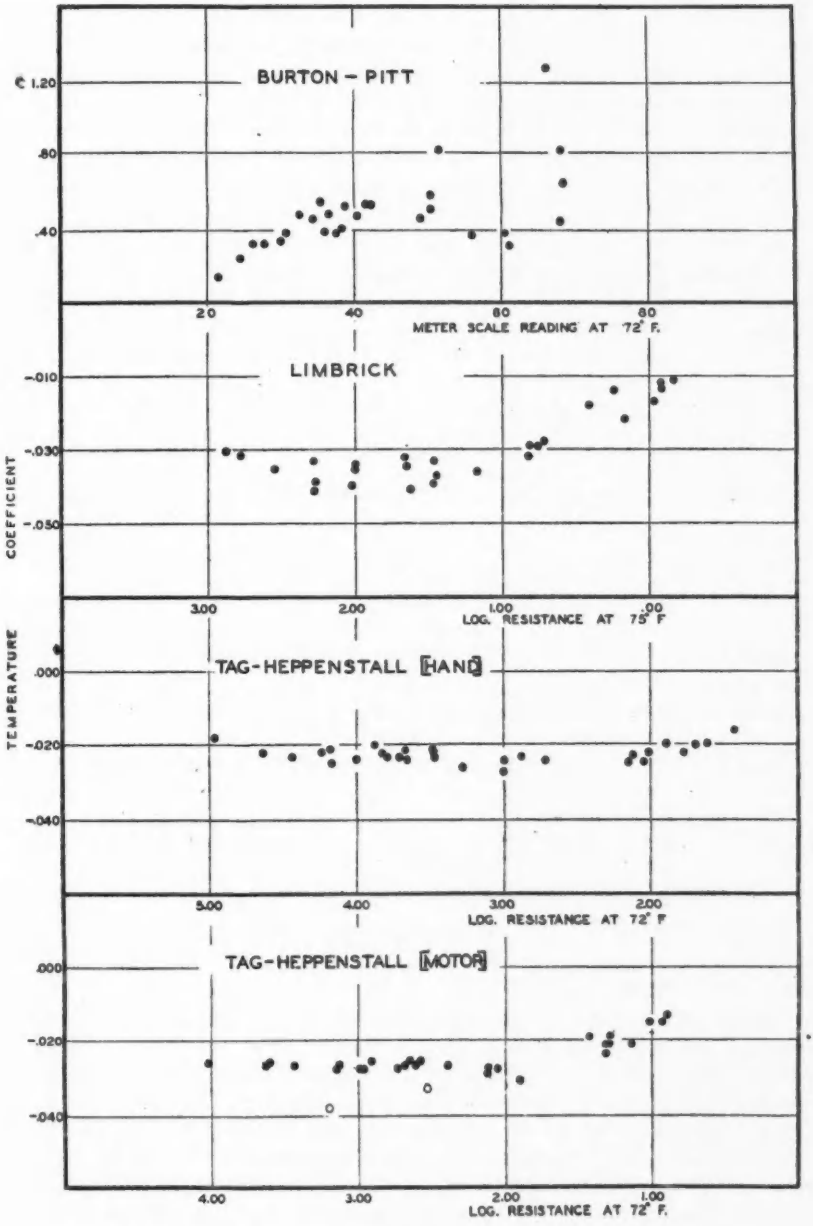

FIG. 3. *Variation of temperature coefficient of wheat—instrument system with moisture content.*

is dependent on the moisture content. The coefficient is positive for the Burton-Pitt, increasing with the meter reading or moisture content of the sample. With the resistance instruments the temperature coefficient in terms of resistance is again negative and the tendency is for this coefficient to increase in absolute magnitude with the resistance, *i.e.*, decrease as the moisture content increases.

Since the temperature coefficient depends on the moisture content of the grain, the total range of the meter readings was divided into smaller ranges over which a common temperature correction might be applied. These ranges, together with the average temperature coefficient applicable to each and the standard error of these average values, are given in Table IV. These values were employed in making subsequent corrections, in connection with

TABLE IV

TEMPERATURE COEFFICIENT OF WHEAT–INSTRUMENT SYSTEM (WHEAT AND METER AT SAME TEMPERATURE)

Meter	Meter range	Temp. coeff. per °F.	Standard error	Unit of measurement
Burton-Pitt	20–30	0.26	0.04	Meter scale division
	30–50	0.46	0.02	
	50–60	0.58	0.09	
	Over 60	0.72	0.14	
Limbrick	3.00–2.50	−0.0323	0.0014	Logarithm of resistance in megohms
	2.50–1.00	−0.0364	0.0008	
	1.00–0.50	−0.0296	0.0008	
	Under 0.50	−0.0153	0.0014	
Tag-Heppenstall (hand)	5.00–2.00	−0.0228	0.0004	Logarithm of resistance in 1000's of ohms
	2.00–1.50	−0.0205	0.0006	
	Under 1.50	−0.0159	0.0013	
Tag-Heppenstall (motor)	4.00–1.50	−0.0274	0.0003	Logarithm of resistance in 1000's of ohms
	1.50–1.00	−0.0202	0.0010	
	Under 1.00	−0.0141	0.0011	

the general reliability tests, for the variations which occurred in the room temperature, since under these conditions the temperature of both the grain and the instruments is affected.

Although the results presented in Table III are, for reasons already given, less precise than those in Table IV, a comparison of these two tables gives some idea of the difference between the temperature coefficient of the wheat only, and that of the instrument and wheat together. The data in the two tables are not averaged over exactly the same moisture ranges, but this is of little consequence compared with the experimental errors in the first experiment. With the Burton-Pitt, within the moisture range of straight and tough wheat where the instrument is reasonably accurate, the coefficient of the wheat only is less than the combined coefficient of the wheat and the instrument, indicating that the meter itself is affected by temperature even

after it has been calibrated and set at the correct sensitivity at each temperature. With the Limbrick, the temperature coefficient of the wheat is on the average only about two-thirds of the combined temperature coefficient. This suggests that the resistances in the instrument also change with temperature, but in the opposite direction, *i.e.*, increasing with temperature, whereas the resistance of the wheat decreases with temperature. Whether or not the difference between the two temperature coefficients can be attributed entirely to the resistance coils is not known. A measurement of the temperature coefficient of a 1-megohm "metallized" type of resistor, similar to those used in this instrument, showed that it was much larger than that of wire-wound resistances, but was still too small to account for the magnitude of the observed effect. It is possible, however, that the temperature coefficient of the metallized resistor increases with the resistance and, since resistances as high as 200 megohms are used, this might account for the temperature coefficient observed. The two temperature coefficients determined for the motor-operated Tag-Heppenstall instrument are essentially the same within experimental error. This might be expected, partly because of the circuit employed, and partly because the resistances are made of manganin, which has an extremely small temperature coefficient.

5. Effect of Humidity

Nothing appears to be known concerning the influence of humidity on these electrical moisture testers. Long exposure of the grain to atmospheres of high or low humidity would naturally change its moisture content, but short exposures to the humidity of the test room should not have any significant effect. Any influence of variable humidity while testing must therefore be attributed to an effect on the instrument. With a meter of the resistance type it is possible that high humidity might decrease the resistance of the surface leakage path over the bakelite or other insulating material between the electrodes. This is especially true when the observed resistances are high, as in the Limbrick. A similar effect is possible but less likely in the dielectric instrument, but even here the humidity is likely to affect the air condenser and the surface of the test condenser. This interfering influence may, however, be removed by making the necessary adjustments of the calibration and sensitivity.

In order to determine the effect of humidity experimentally, further portions of the samples employed in the temperature experiments were tested in the Burton-Pitt, Limbrick, and motor-operated Tag-Heppenstall instruments. Relative humidities of 20, 30, 40, 50, 60 and 70% at a temperature of 72° F. were employed, and the results are shown in Fig. 4. Those obtained with the Limbrick apply at 75° F., since the grain is warmed somewhat by grinding. In all cases any effect due to small variations in temperature was removed by applying the temperature corrections already discussed.

It is apparent from Fig. 4 that the effect of humidity is small compared with that of temperature. Close examination also shows that the effect varies somewhat with the moisture content of the wheat, and in order to study this more exactly the approximate humidity coefficient was determined graphically for each sample and averaged separately for the "straight", "tough", and "damp" moisture classes. The results for all three meters are shown in Table V.

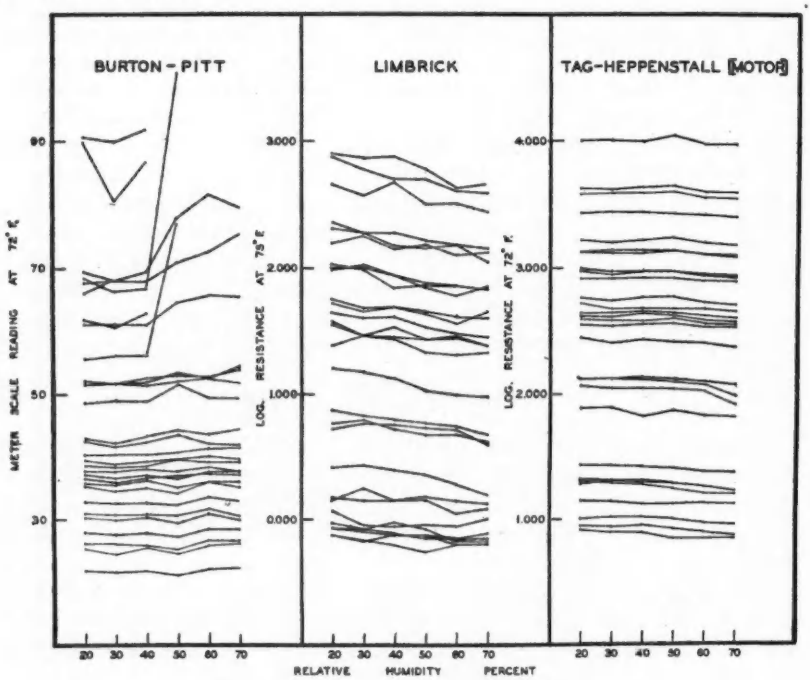

FIG. 4. *Effect of humidity on meter reading.*

TABLE V

HUMIDITY COEFFICIENT OF WHEAT-INSTRUMENT SYSTEM
(WHEAT AND METER AT SAME HUMIDITY)

Meter	Humidity coefficient per 1% change in relative humidity at 72° F.			Unit of measurement
	Straight*	Tough*	Damp*	
Burton-Pitt	0.0089	0.0137	0.1782	Meter scale division
Limbrick	−0.00356	−0.00331	−0.00198	Logarithm of resistance in megohms
Tag-Heppenstall (motor)	−0.00082	−0.00110	−0.00135	Logarithm of resistance in 1000's of ohms

* *For exact definition of moisture limits see Table I, previous paper (5).*

With the Burton-Pitt an increase in humidity gives higher readings, the increase being greater with grain of high moisture content. Owing to the fact, previously cited, that this instrument yields extremely erratic results on all samples giving a deflection of over 50 scale divisions, the coefficient calculated for damp grain is subject to some uncertainty. The effect of humidity on the Limbrick is relatively high at low moisture contents and decreases in magnitude as the moisture in the wheat increases. As the resistance to be measured in this instrument is high, the humidity effect may be due to an increased tendency toward surface leakage as the humidity increases. Surface leakage also offers an explanation for the higher humidity coefficient at low moisture contents, *i.e.*, higher resistances. The motor-operated Tag-Heppenstall has the smallest humidity coefficient of any of the three meters studied. The observed effect of humidity on this instrument can hardly be attributed to surface leakage as in the Limbrick, since the resistance measured is much lower. Furthermore, the effect increases with the moisture content of the wheat, a trend for which no explanation can be offered.

6. Calibration and Accuracy of Meters

Further subsamples of the 300 hard red spring wheat samples already referred to (5), were employed to determine the calibration and accuracy of the various meters. The temperature coefficients, described in § 4, were used to correct the observed readings for the small temperature fluctuations occurring in the conditioned room in which the tests were made. A standard temperature of 72° F. was adopted, with the usual correction of +3° in the Limbrick, to allow for the heating of the grain in grinding. Correction for the small fluctuations in relative humidity, from the standard 40% which occurred, was unnecessary since the humidity coefficients are so small.

Briefly the method of dealing with the results consisted of making the temperature corrections, calculating the standard error of observation ("experimental error") from the difference between the duplicate meter readings, and then plotting the vacuum oven moisture content against either the meter scale reading or, in certain resistance instruments, against the logarithm of some convenient multiple of the observed resistance. It was found that at moisture contents higher than about 17.0%, the relationship deviated significantly from the linearity observed at lower moisture contents, and as the errors of prediction were also somewhat larger at the high moisture contents, a separate curve was employed to represent the results in this moisture range. Since other investigators (3, 4) have shown that naturally damp grain behaves differently in certain electrical moisture meters from grain artificially dampened shortly before the tests, these two classes of damp wheat were analyzed separately, in spite of the fact that the artificially dampened samples had been tempered about a month before testing.

All the calibration curves were fitted by the method of Least Squares. The observed standard error of prediction of vacuum oven moisture content was computed, for the mean of duplicate determinations, from the sum of

the squares of the deviations of the observed values from the fitted curve. The net error of prediction was obtained from the observed error by allowing for the sampling error and the experimental error of the vacuum oven method.

The standard error of the duplicates, or "experimental error", was obtained in terms of meter scale reading or logarithm of the observed resistance, these being converted into terms of moisture by means of the appropriate calibration equation. When this was parabolic, the average moisture difference corresponding to the given instrumental deviation was computed from the average value of the first derivative.

Davies Meter

Preliminary experiments with the Davies meter demonstrated that it would be necessary to use three different sensitivities in order to obtain satisfactory readings on a series of samples of different moisture content. The only method of adjusting the sensitivity on this relatively simple instrument was to change the voltage. Sensitivity 1 employed a voltage of 100 and was necessary to give readable deflections with grain below 16.0% moisture. Sensitivity 2 corresponded to full-scale (100) deflection on the galvanometer with the standard resistance in the circuit, *i.e.*, a voltage of 46.86. Sensitivity 3 corresponded to a deflection of 30 scale divisions with the standard resistance in the circuit, a voltage of 14.0. Wherever possible the intermediate sensitivity was used, since this gave the closest approximation to the test conditions outlined by the manufacturers. Sensitivity 1 was used only with samples giving a scale deflection of less than 5, and Sensitivity 3 only with samples giving over full-scale deflections when the instrument was operated at intermediate sensitivity.

An examination of the results obtained showed that the meter was quite inaccurate and unsuitable for measuring the moisture content of wheat, the standard error of the duplicates ("experimental error") alone, for all samples tested at the intermediate sensitivity, being 5.9% of the average meter scale reading. Under these conditions it was not worthwhile converting the meter readings to resistance, fitting a curve to the points mathematically, or obtaining additional data on the effect of temperature. The results obtained are shown in Fig. 5 in which the vacuum oven moisture is plotted against the meter scale reading at the three sensitivities.

It is evident that even at the highest voltage (Sensitivity 1) the meter was not capable of distinguishing between "straight" and "tough" wheat, *i.e.*, below and above 14.5% moisture, since nearly all of the samples below 16.0% moisture gave deflections of less than 5 scale divisions. This alone renders it entirely unsuitable for commercial tests on wheat, even if the instrumental readings were reliable, and the large experimental error at Sensitivities 2 and 3 show that this is not so. The data plotted in Fig. 5 were not corrected for temperature variations, but as these never exceeded 3° or 4° F. such corrections would have little effect on the observed variability.

The large experimental error observed at the intermediate sensitivity suggests that the design of the test cell is faulty, for the scale deflections in this range were large enough to permit the meter to be read with reasonable accuracy. It is probable that the range of the instrument could be increased by the use of a larger test cell and a more sensitive galvanometer. In order

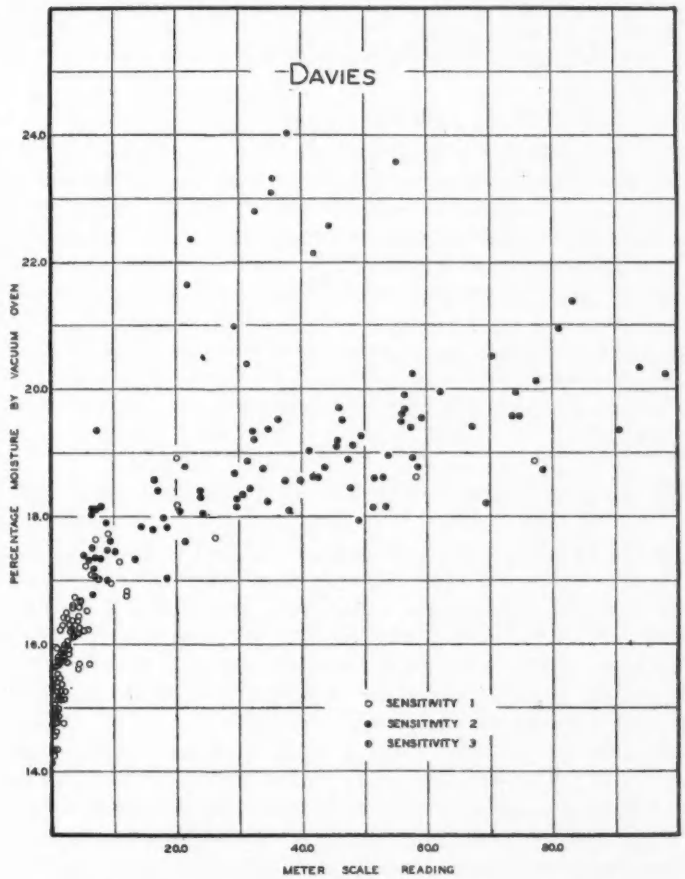

FIG. 5. *Relation between moisture content of wheat and Davies meter reading.*

to cover the wide range of moisture content experienced commercially, however, several sensitivities would still be required, together with a corresponding number of calibration charts. This is necessitated by the fact that an electrical measuring instrument such as a galvanometer, when used directly without a shunt or adjustable resistances, follows Ohms' law, *i.e.*, a rectangular hyperbolic relationship between deflection and resistance at constant voltage. On the other hand, the change of resistance of grain with increasing moisture

content is logarithmic (see Figs. 7, 8 and 9), and when a galvanometer is used directly to observe such resistances, the deflections at high resistance (low moisture content) will all be too small to permit distinction between two samples of slightly different moisture content, while at high moisture contents (low resistance) the meter will show enormously increased deflections for negligible differences in moisture content. An additional disadvantage arises from the fact that at high voltages there is a greater possibility of errors due to polarization.

Burton-Pitt Tester

As the result of several preliminary experiments, a sensitivity of 90 scale divisions, when the constant capacity condenser was in the circuit, was selected for the main series of experiments with the Burton-Pitt tester. At this sensitivity, five scale divisions corresponded to approximately 1.0% change in moisture content, and it was felt that had a lower sensitivity been employed, the errors of reading the milliammeter might have affected the accuracy of the results. A full-scale deflection of 100 divisions on the other hand would have limited the measurable moisture range to about 21.5%, and as few samples of higher moisture occur in commercial practice, it would have been difficult to establish a reliable supplementary calibration curve at a lower sensitivity.

The results obtained are shown in Fig. 6, and it is evident, as in the temperature and humidity studies, that the meter is decidedly erratic at deflections greater than 50 scale divisions, corresponding to moisture contents above 17%. The curve fitted to the points at lower moisture contents was parabolic, the equation being $M_V = 6.87 + 0.279x - 0.00152x^2$, where M_V is the moisture content by the vacuum oven, and x the Burton-Pitt reading in scale divisions at a sensitivity of 90. This slightly curved relationship between moisture content and scale reading was observed by Coleman (4), working with the D-K apparatus, which is also of the dielectric type, although Burton and Pitt (3) claim the existence of a linear relationship.

The standard errors of the mean of duplicate determinations made with this instrument ("experimental errors") were as follows: 0.06% moisture over the moisture range 11.0 to 17.0% covered by the curve; and 0.10% for all samples of higher moisture content. The experimental error at low moisture contents is therefore only slightly higher than those observed with the analytical methods, but at high moisture contents the meter is definitely less consistent. Apparently the circuit, or some part of the instrument, is too unstable to give constant results at scale deflections over 50. The observed standard error of prediction of vacuum oven moisture over the range covered by the curve was 0.55% moisture, and 0.54% after allowing for the proportion of the variance due to the sampling error and the experimental error of the vacuum oven determination. The error of prediction of moisture content is therefore much larger than the "experimental error" estimated from duplicate determinations on the same sample, a result similar to the findings with the analytical methods (5). The high error of prediction

shows that this meter is relatively inaccurate for determining the moisture content of wheat at moisture contents below 17.0%, and at higher moisture contents it is of no practical utility.

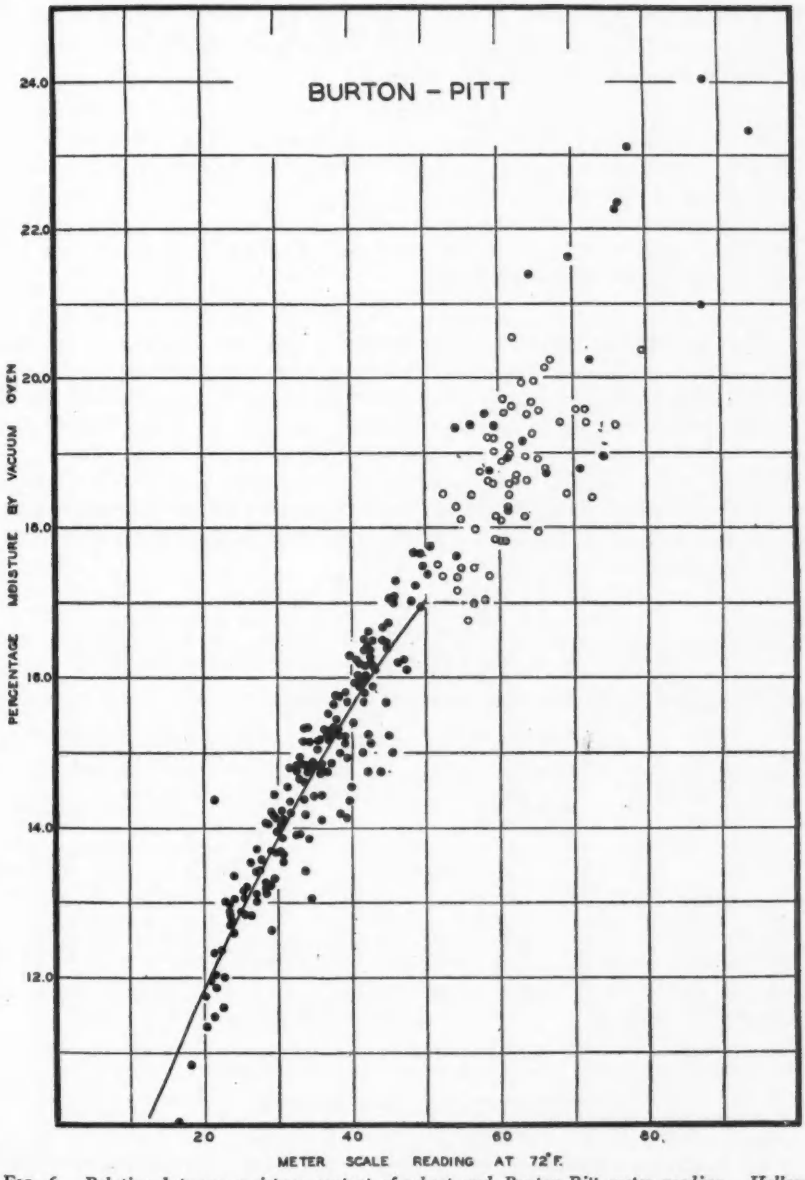

FIG. 6. *Relation between moisture content of wheat and Burton-Pitt meter reading. Hollow circles represent artificially dampened samples.*

Limbrick Tester

The Limbrick tester was used at its maximum sensitivity, *i.e.*, full-scale deflection on minimum resistance. Under these conditions its upper moisture limit was about 21.5% moisture, and its lower limit about 11.5% moisture. By altering the setting of the sensitivity the instrument can be made to measure grain of higher moisture content, but it is impossible to increase the sensitivity further to include drier grain.

The moisture content of the samples falling within the range of this meter is plotted against the logarithm of the resistance in megohms at 75° F. in Fig. 7. Four curves were fitted to the results, one representing the linear relationship at moisture contents below about 17.0%, another (broken line) the relationship with all samples of higher moisture content, and, as the artificially and naturally damp samples gave significantly different results, separate curves are shown for these.

It is evident that with grain of high moisture content the relationship between percentage moisture and resistance is parabolic, a given increment of moisture causing a progressively smaller change in resistance. Owing to the relatively small number of samples of high moisture content, the curves are determined with some uncertainty at the ends of the range, and do not meet exactly the curve obtained at lower moisture contents. Both the naturally and artificially damp samples show a similar curved relationship, the main difference being that the position of the curve is lower with artificially dampened samples. This point is discussed in greater detail towards the end of this section.

TABLE VI

EXPERIMENTAL ERROR, CALIBRATION EQUATIONS, AND OBSERVED AND NET STANDARD ERROR OF PREDICTION OF VACUUM OVEN MOISTURE CONTENT OF WHEAT BY THE LIMBRICK MOISTURE TESTER

Moisture range	Experimental error (standard error of duplicates), % moisture	Calibration equation*	Standard error of prediction	
			Observed moisture, %	Net moisture, %
11.5 to 17.0%	0.08	$M_V = 18.39 - 1.96 \log. R$	0.40	0.38
17.0 to 21.5% (all samples)	0.09	$M_V = 19.43 - 4.65 \log. R + 2.32 (\log. R)^2$	0.51	0.49
17.0 to 21.5% (naturally damp)	0.07	$M_V = 19.76 - 4.92 \log. R + 2.39 (\log. R)^2$	0.48	0.46
17.0 to 21.0% (artificially damp)	0.10	$M_V = 19.36 - 4.39 \log. R + 1.71 (\log. R)^2$	0.46	0.44

Standard errors apply to mean of duplicates.

* M_V = *moisture content as determined by vacuum oven.*

R = *resistance in megohms.*

The experimental error, calibration equation, and observed and net error of prediction applicable to each series, are given in Table VI. The net error

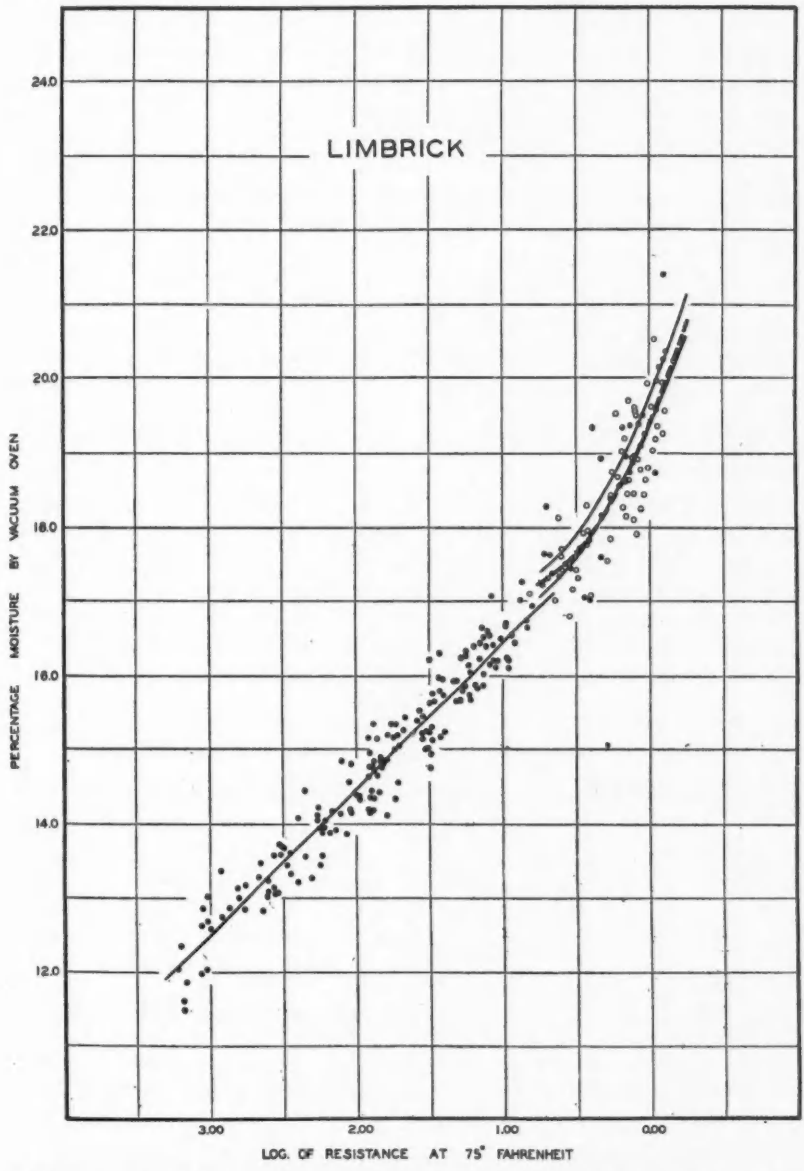

FIG. 7. *Relation between moisture content of wheat and logarithm of resistance in megohms. Limbrick meter. Hollow circles represent artificially dampened samples.*

strictly attributable to the instrument is estimated by allowing for the proportion of the residual variance due to sampling error and experimental error of the vacuum oven. The "experimental error" at low moisture contents is actually somewhat higher in terms of resistance than at high moisture content, a result which can doubtless be attributed to the difficulty of measuring the extremely high resistances accurately. The error of prediction is again much larger than the experimental error, and is somewhat larger for samples above 17.0% moisture. The slightly smaller error of prediction with the artificially dampened samples can doubtless be partially attributed to the fact that they fall in a lower moisture range than the naturally damp samples.

Hand-operated Tag-Heppenstall Meter

The Tag-Heppenstall instruments employ an Ayrton shunt, and are capable of covering a wide range of moisture content. Other than the use of the appropriate shunt stud there is no method provided for altering the sensitivity. The hand-operated instrument was operated at the roll-setting nearest to 40/1000 in., the spacing recommended in the manufacturer's instructions.

The results obtained are shown in Fig. 8, in which the vacuum oven moisture content is plotted against the logarithm of the resistance in thousands of ohms. They show the same general characteristics as those with the Limbrick, namely, a linear relationship at moisture contents up to about 17.5%, and then a parabolic relationship at higher moisture contents. As the artificial and naturally damp samples gave significantly different results, separate curves are shown for these. Again the curves do not meet exactly,

TABLE VII

Experimental error, calibration equations, and observed and net standard error of prediction of vacuum oven moisture content of wheat by the hand-operated Tag-Heppenstall moisture meter

Moisture range	Experimental error (standard error of duplicates), % moisture	Calibration equation*	Standard error of prediction	
			Observed moisture, %	Net moisture, %
11.0 to 17.5%	0.04	$M_V = 23.78 - 2.46 \log R$	0.42	0.40
17.5 to 24.0% (all samples)	0.05	$M_V = 28.77 - 7.39 \log R + 1.15 (\log R)^2$	0.46	0.44
17.5 to 24.0% (naturally damp)	0.06	$M_V = 28.78 - 7.38 \log R + 1.18 (\log R)^2$	0.65	0.64
17.5 to 21.0% (artificially damp)	0.05	$M_V = 26.84 - 5.54 \log R + 0.71 (\log R)^2$	0.38	0.35

Standard errors apply to mean of duplicates.

* M_V = *moisture content as determined by vacuum oven.*
R = *resistance in 1000's of ohms.*

owing to the uncertainty which is inevitable at the end of the range with the small number of samples in the high moisture, naturally damp group. The errors and equations applicable to these curves are given in Table VII.

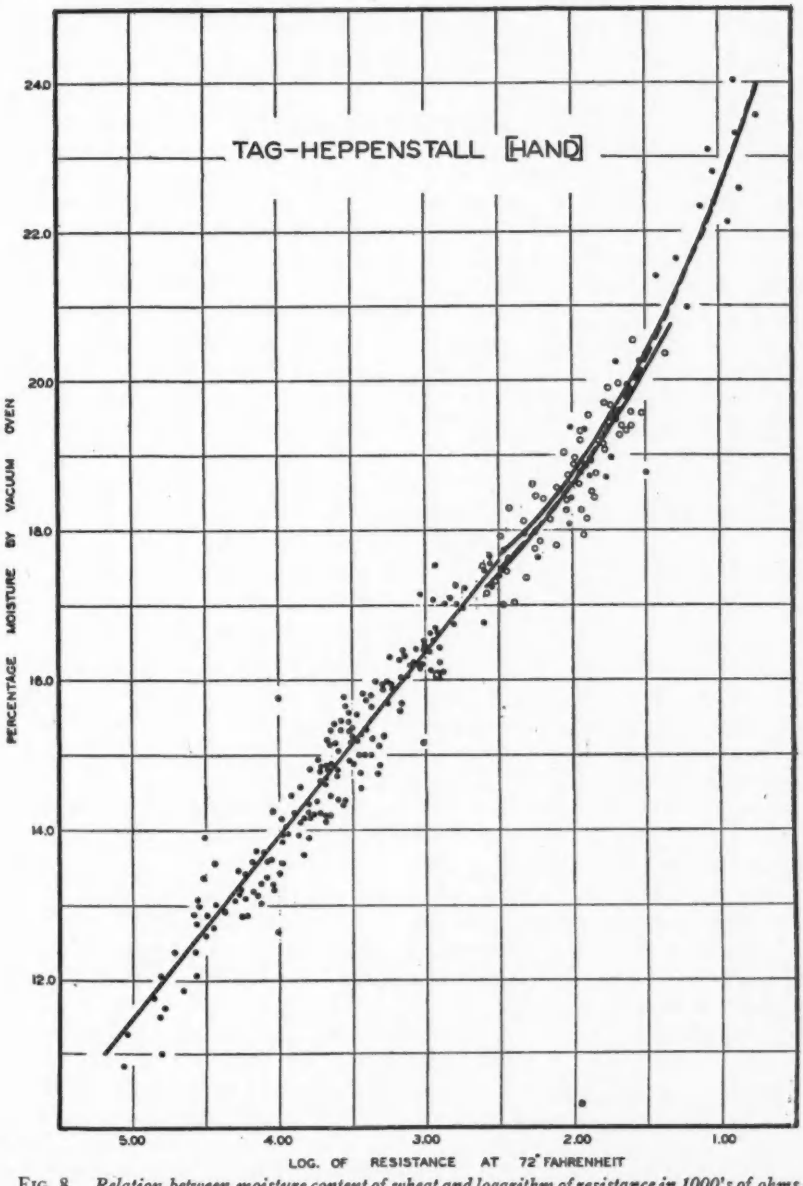

FIG. 8. *Relation between moisture content of wheat and logarithm of resistance in 1000's of ohms. Hand-operated Tag-Heppenstall meter. Hollow circles represent artificially dampened samples.*

The "experimental error", in terms of moisture, of this instrument is somewhat lower than that observed with the preceding meters. It seems probable that larger rollers, or a different roll spacing, would give even smaller experimental errors, for it was observed, during the course of the experiments, that the wheat did not feed into the rolls uniformly at the roll spacing used.

The net standard error of prediction, after allowing for the sampling error and the experimental error of the vacuum oven determination, is slightly higher than for the Limbrick instrument in the linear part of the moisture range. It is evident from Fig. 8 that a few of the points show a considerable divergence from the line, and these contribute considerably to the variance. Figs. 7, 8 and 9 also reveal that the upper moisture limit varied somewhat in the experiments with the different instruments. Thus 21.5% was the maximum moisture content that could be measured with the Limbrick instrument at the sensitivity used, while the Tag-Heppenstall instruments could be used for all samples, the highest moisture content encountered being about 24.0%. Since the meters all tend to become less accurate as the moisture content increases, the range of moisture contents included in this "damp" class must be considered in relation to the standard error of prediction for this range. In spite of the higher average moisture content of the samples tested in the damp range with the hand-operated Tag-Heppenstall meter, however, the error of prediction for all samples is lower than that obtained with the Limbrick instrument. The lower error of prediction with artificially damp samples as compared with the naturally damp group may again be partially explained by their lower average moisture content.

Motor-operated Tag-Heppenstall Meter

The roll spacing of the motor-operated Tag-Heppenstall was adjusted to 40/1000 in., as required by the instructions, by means of the shims provided. The calibration curves, shown in Fig. 9, are again of essentially the same type as those obtained with the hand-operated model and the Limbrick. There was again a significant difference between the results with artificial and naturally dampened samples. The calibration equations, and the errors applicable to each, are given in Table VIII. The experimental errors were lower with this instrument than with any of the other meters or analytical methods studied. Within the linear moisture-resistance range, this meter is much the most accurate of those tested, the net standard error of prediction being 0.16% moisture. The error of prediction for all samples of higher moisture content was larger than for either the Limbrick or hand-operated Tag-Heppenstall. It should be mentioned, however, that as the upper moisture limit of the Limbrick is lower than that of the Tag-Heppenstall meters a number of the wettest samples studied could not be tested in the Limbrick. As the accuracy of all the meters decreased with increasing moisture content this may account, in part, for the larger errors observed in the motor Tag-Heppenstall as compared with the Limbrick meter. There is no evident reason however for the motor-model being less accurate in this

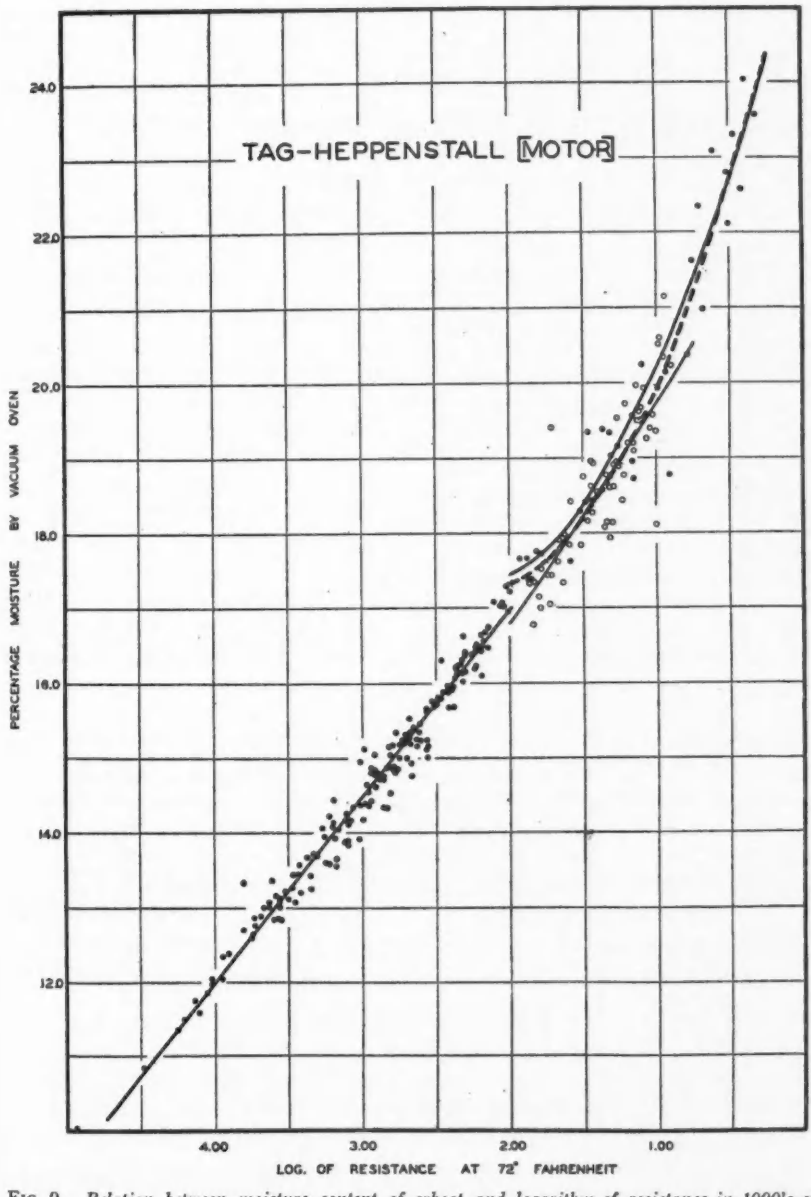

FIG. 9. *Relation between moisture content of wheat and logarithm of resistance in 1000's of ohms. Motor-operated Tag-Heppenstall meter. Hollow circles represent artificially dampened samples.*

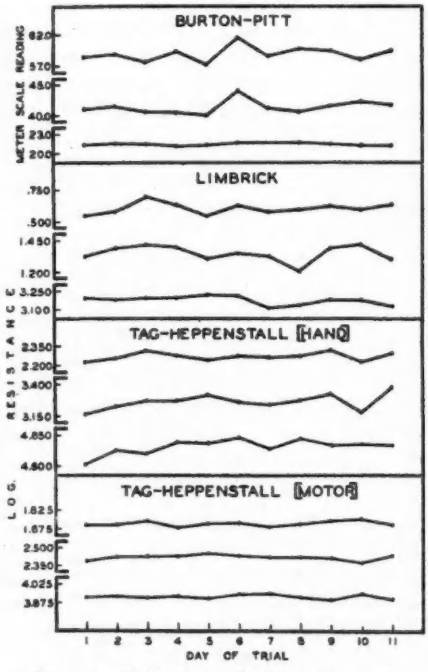

FIG. 10. *Daily fluctuations in meter results.*

range than the hand-operated type, except that two of the points, as shown in Fig. 9, exhibit considerably more departure from the curves than any of the others. The lower error of prediction with artificially damp samples may again be explained by the lower average moisture content of the former.

DAY-TO-DAY VARIATIONS

Subsamples of three large samples, one from each of the straight, tough, and damp, moisture classes, were tested daily in all meters in order to determine the extent to which the results were affected by daily fluctuations. The observed meter reading on these three samples is shown plotted against the day of test, for all meters except the Davies, in Fig. 10. Where the curves rise or fall together on a particular day, this is an indication of

TABLE VIII

EXPERIMENTAL ERROR, CALIBRATION EQUATIONS, AND OBSERVED AND NET STANDARD ERROR OF PREDICTION OF VACUUM OVEN MOISTURE CONTENT OF WHEAT BY THE MOTOR-OPERATED TAG-HEPPENSTALL MOISTURE METER

Moisture range	Experimental error (standard error of duplicates), % moisture	Calibration equation*	Standard error of prediction	
			Observed moisture, %	Net moisture, %
11.0 to 17.0%	0.02	$M_V = 21.93 - 2.48 \log. R$	0.21	0.16
17.0 to 24.0% (all samples)	0.03	$M_V = 26.21 - 8.08 \log. R + 1.82 (\log. R)^2$	0.58	0.56
17.0 to 24.0% (naturally damp)	0.03	$M_V = 26.07 - 7.48 \log. R + 1.58 (\log. R)^2$	0.68	0.67
17.0 to 21.0% (artificially damp)	0.03	$M_V = 23.01 - 3.44 \log. R + 0.17 (\log. R)^2$	0.46	0.43

Standard errors apply to mean of duplicates.

* M_V = *moisture content as determined by vacuum oven.*
R = *resistance in 1000's of ohms.*

TABLE IX

EFFECT OF DAILY FLUCTUATIONS IN THE VACUUM OVEN AND METER RESULTS

Meter	Standard error of prediction of vacuum oven moisture in range 11.0 to 17.0%	
	Calculated around general mean, % moisture	Calculated around daily means, % moisture
Burton-Pitt	0.54	0.50
Limbrick	0.38	0.36
Tag-Heppenstall (hand)	0.40	0.38
Tag-Heppenstall (motor)	0.16	0.14

a daily fluctuation, while divergent results can be attributed to experimental or sampling errors. The curves suggest the existence of slight daily fluctuations with all meters except the motor-operated Tag-Heppenstall. (Note Burton-Pitt results sixth day; Limbrick results fifth day; and hand-operated Tag-Heppenstall results first day). Nevertheless, an analysis of variance showed that these systematic daily fluctuations could not be judged significantly greater than the erratic fluctuations, on the number of observations available.

It has already been shown (5) that there are significant fluctuations in the vacuum oven results from day to day. In obtaining the net error of prediction applicable to the meters, as given earlier, the experimental error of the vacuum oven and the sampling error only were allowed for. The effect of daily fluctuations in both the vacuum oven and the meter under test can, however, be eliminated by calculating the variance and covariance around the daily means, instead of around the means for the entire series. When this is done the standard error of prediction for the linear part of the range below about 17.0% moisture was reduced as shown in Table IX. Although the reduction in each case is statistically significant, the effect from a practical point of view is negligible. Whether this reduction in the standard error can be attributed entirely to the daily variations in the vacuum oven, or whether it is also due in part to daily fluctuations in the meters, cannot be said with assurance, but it seems likely that part of the reduction in the error of the Burton-Pitt meter at least, is due to the presence of daily fluctuations in the results by that instrument.

EFFECT OF ARTIFICIAL DAMPENING

Since the artificially dampened wheat had been allowed to stand about a month between tempering and the performance of the tests, it was felt that these samples should behave as naturally damp in the electrical testers. Nevertheless, since Coleman (4) had shown that artificially dampened samples do not give the same results as naturally damp samples, at least for several days after tempering, the results from the two classes of wheat were examined separately. It was found that in the three most accurate meters there was a significant difference, the artificially dampened samples exhibiting on the

average a slightly higher conductivity than naturally damp samples of the same apparent moisture content. As, however, the natural and artificially dampened samples were not tested on the same days, the situation may be complicated by the effects of daily fluctuations. The presence of small but significant fluctuations affecting all the results obtained on a particular day has already been demonstrated in the straight and tough samples (Table IX) when tested by any of the foregoing meters. A more detailed examination of the results with these straight and tough samples revealed that those tested on the same days as the artificially dampened also showed a slightly higher conductivity, when reduced to a common moisture basis, than those tested on the days when naturally damp samples were employed. As this differentiation is common to all three meters, daily fluctuation in the vacuum oven results suggests itself as the underlying cause. It thus seems likely that part, if not all, of the observed difference between the naturally damp and artificially dampened samples may be attributable to similar daily fluctuations.

7. Effect of Grade and Variety of Wheat

Burton and Pitt (3) state that they are confident that the relationship which they obtained between moisture content and current strength (scale reading) holds for all ordinary grades and varieties of wheat, but also state that for accurate work it will be necessary to calibrate the apparatus for the particular variety tested. In addition to the possibility of a different calibration curve being required for different grades of wheat, it was felt that the presence of a number of lower grade samples might add to the variability, since grain may be of low grade for many different reasons.

In order to study the effect of grade, the 37 samples of grade No. 4 Northern or lower, which occurred within the linear range below 17.0% where the meters are most accurate, were compared with 37 samples grading No. 1 Hard, No. 1 or No. 2 Northern. The latter were selected to have about the same moisture content as the low grade samples, and the same number of high and low grades were selected from each day of test so as to equalize any effect of daily fluctuations. The data, plotted in Fig. 11, show no evidence of the need of a separate calibration chart for the high and low grades nor do they indicate that the low grade were significantly more variable than the high grade samples. These conclusions were confirmed by an analysis of variance. To obtain this result with the Tag-Heppenstall instruments is rather surprising, since the less uniformly sized kernels common to the lower grades might reasonably be expected to give different results when the same roll spacing is used throughout. However, the crop year 1933-34 provided relatively few types of low grade wheat such as frozen, rusted, sprouted or artificially dried, which occur in certain seasons. It should be mentioned, moreover, that all of the samples were carefully cleaned before testing, and the presence of dirt, weed seeds or other impurities may affect the accuracy of the instruments in commercial practice.

The study of varieties was limited to a comparison of Garnet with the hard red spring wheat varieties represented in the 300 samples employed in the general reliability test, owing to the difficulty of obtaining pure varieties having a wide range of moisture content. This variety, since it has a distinctly

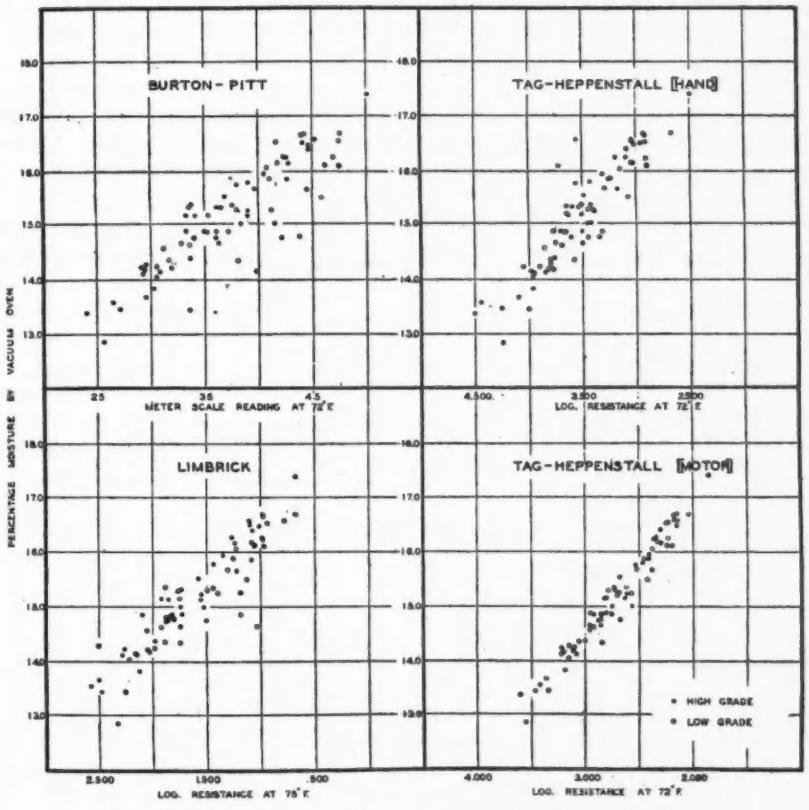

FIG. 11. *Comparison of meter results with high- and low-grade wheats.*

harder kernel than the other spring wheats tested, should show whether any difference is likely to occur in the behavior of varieties in the electrical moisture meters.

The 28 Garnet samples used all fell within the straight and tough moisture classes. The results obtained with the four moisture meters are plotted in Fig. 12 together with the calibration curves already obtained from the general reliability test. It is evident that this curve fits the points for all instruments, within the usual variation, except the hand-operated Tag-Heppenstall. With this instrument the resistance, at a given moisture content, appears to be slightly higher for Garnet than for the other samples. It has already been men-

tioned that in the earlier tests the wheat did not feed into the rollers of this instrument in an entirely uniform manner at the roll spacing recommended. This effect was even more pronounced with the harder kernelled Garnet, and the number of kernels caught between the rolls at any instant was probably smaller than with the softer wheats, thus accounting perhaps for the slightly higher resistance observed. Otherwise there is no evidence to indicate that a different calibration curve is required for different spring wheat varieties.

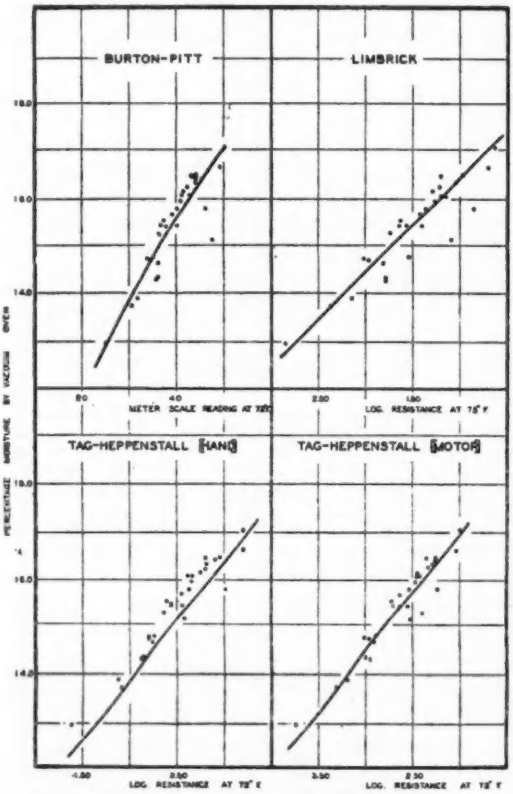

FIG. 12. *Comparison of meter results with Garnet and other hard red spring wheat varieties.*

Although no extensive study of the meter adjustments was contemplated, it seemed advisable to give the roll spacing in the hand-operated Tag-Heppenstall meter some consideration, since it was observed that the fluctuations of the microammeter needle were much greater with Garnet than with the other hard red spring wheat varieties, a finding which might be attributed to the uneven manner in which this wheat fed through the rolls. The spacing is adjusted by means of an eccentric arm with settings numbered from 1 to 5, the distance between the rolls increasing with the numbers. Setting No. 3, found to be $40/1000 \pm 1/1000$ in. was used in all previous experiments, in accordance with the manufacturer's recommendations. In a supplementary experiment, settings 4 and 5 were also used, though the spacings these provide are not known. The standard error of the mean of duplicates with the Garnet samples at the above settings was found to be: No. 3, 0.12% moisture; No. 4, 0.08% moisture; and No. 5, 0.06% moisture. It is evident that the wider spacings give better results with this variety, and it is probable that a somewhat similar result would be obtained with other spring wheat varieties. The roll spacing employed, and meter adjustments generally, should be subjected to critical study, as the accuracy of some of the meters might thus be improved.

8. Tests with Wheat of Low Moisture

Although the calibration curves given earlier cover the moisture range of main commercial importance, a few experiments were performed with very dry wheat in order to determine the lowest moisture content the meters were capable of measuring, and also to ascertain whether the calibration curves already determined could be extrapolated to include such low moisture contents. Only the Burton-Pitt and the two Tag-Heppenstall meters were employed in this experiment, the lower limit of the Davies and Limbrick being already attained in the calibration experiments.

The results obtained are shown in Fig. 13, the points indicating the observed values, while the lines are an extrapolation of the calibration curve previously given, obtained by substituting the observed resistances in the

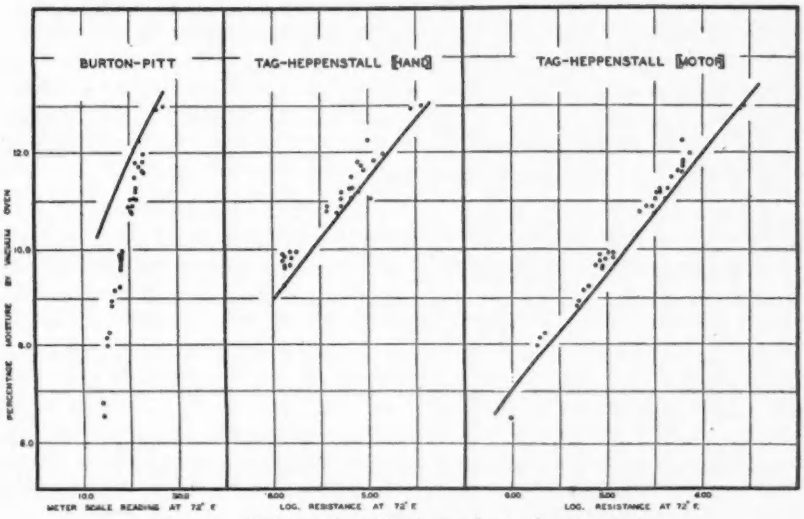

FIG. 13. *Meter results with wheat of low moisture content.*

calibration equations. It was found that the hand-operated Tag-Heppenstall was not capable of determining moisture contents lower than about 9.0%, but the motor-operated model could be read at moisture contents as low as 7.0%, since the roller electrodes are much larger, and the observed resistances proportionately smaller.

The Burton-Pitt gave appreciable deflections even on the driest wheat employed, but it is evident from Fig. 13 that the points do not follow the curve deduced from wheat of higher moisture contents, a given decrement of moisture causing progressively smaller change in the meter reading. This decreasing sensitivity makes it probable that the error of prediction at moisture contents below about 10% would be relatively large.

The results with the two Tag-Heppenstall instruments follow closely the calibration curve obtained at higher moisture levels, but the points are in

general above the line. It is possible that this may represent a real difference, *e.g.*, these dry wheats may not feed into the rollers as uniformly as the softer kernels of moister wheat, but it may also be explained by daily variations in the vacuum oven, as previously noted, since all these samples were tested on one day.

9. Corrections for Variations in Temperature and Humidity

The temperature coefficients in terms of meter reading and logarithm of resistance have already been given in Tables III and IV. In commercial practice, it is more convenient (though less accurate if the calibration is non-linear) to present these temperature coefficients in terms of correction values, showing the amount of moisture to be added or subtracted for each degree F. the temperature is below or above that at which the calibration curve or table is applicable. Since the temperature coefficient and the relation between meter reading, or resistance, and the moisture content both vary with the moisture content, it is necessary to give the correction applicable to different moisture ranges separately. The average temperature coefficients for straight, tough and damp grain respectively were therefore computed from the data presented earlier in Table IV, and are summarized in Table X.

It is evident that the temperature correction applicable to the wheat-instrument system increases with increasing moisture content in the Burton-Pitt and hand-operated Tag-Heppenstall, while it tends to decrease with moisture content in the Limbrick, and is remarkably constant throughout the entire moisture range with the motor Tag-Heppenstall meter. The temperature correction applicable to the wheat only, is, for reasons already given, somewhat less precisely determined. Nevertheless, there is no doubt that these two corrections are different in both the Burton-Pitt and Limbrick instruments, where the correction for the wheat only is little more than half that applicable to the wheat and the instrument. There is little difference between the two corrections for the motor Tag-Heppenstall instrument, indicating that the meter itself is little affected by temperature. This finding doubtless applies to the hand-operated model also, since the meter unit is the same.

The question arises as to the temperature range over which these corrections may be applied. The corrections for the wheat–instrument system were determined over the range 60° to 90° F., but since they are linear for the better resistance type meters, they may with reasonable assurance be applied over any range likely to be encountered in practice. The standard error of these corrections for the resistance instruments in the straight and tough moisture ranges is usually not greater than about $\pm 0.001\%$ moisture per °F. (see Table IV), so that they are accurate enough to be applied over a $\pm 50°$ F. range without introducing an error greater than 0.05% moisture. For the Burton-Pitt, the standard error of the corrections is such that the recorded values can only be used over a range of about $\pm 10°$ F. if the same accuracy is required. The corrections for variable wheat temperature only, in the Burton-Pitt and Limbrick instruments, should not be applied over a

greater range than about ±10° F. owing to their uncertainty. With the Tag-Heppenstall instruments the two temperature corrections are so nearly the same that the correction for the wheat–instrument system could be applied to the wheat alone over a range of ±10° F. without introducing significant error. The superiority of the Tag-Heppenstall instrument over the others in this regard is evident.

When an accurate result is required in commercial practice, the grain should be allowed to stand in the test room until it has attained approximately the temperature of the instrument, before the determination is made. The temperature of the wheat should be taken, and as it will then be within a few degrees of the temperature of the room and instrument, the temperature correction for the wheat–instrument system can be used to correct the results without significant error. No attempt should be made, in accurate work, to apply the temperature corrections for the grain alone over a range of more than 10° F., for not only are they themselves uncertain for larger temperature ranges, but difficulty will be experienced in determining the temperature of the grain accurately. It is evident from Table X that an error of 1° F. corresponds to about 0.05% moisture, and it is difficult to measure the temperature of grain which differs from the surrounding atmosphere by more than 10° F. with this degree of accuracy.

The corrections for humidity variations were computed from the humidity coefficients in the manner previously described, and are also given in Table X.

TABLE X

TEMPERATURE AND HUMIDITY CORRECTIONS IN TERMS OF PER CENT MOISTURE

Meter	Standard temperature, ° F.	Correction in terms of per cent moisture for each degree F. above or below the standard temperature					
		Straight		Tough		Damp	
		Wheat and meter	Wheat only	Wheat and meter	Wheat only	Wheat and meter	Wheat only
Burton-Pitt	72	0.071	0.041	0.081	0.047	—	—
Limbrick	75	0.069	0.031	0.067	0.040	0.052	0.037
Tag-Heppenstall (hand)	72	0.054	—	0.057	—	0.066	—
Tag-Heppenstall (motor)	72	0.067	0.060	0.068	0.060	0.068	0.068
	Standard humidity at 72° F., %	Correction in terms of per cent moisture for each 10% change in relative humidity above or below standard humidity					
Burton-Pitt	40	0.017	—	0.021	—	—	—
Limbrick	40	0.070	—	0.065	—	0.060	—
Tag-Heppenstall (motor)	40	0.020	—	0.027	—	0.046	—

NOTE: *Corrections are to be* added *if the temperature or humidity are below the standard, and* subtracted *if above the standard.*

As variations in the humidity have a much smaller effect on the results, the corrections given apply to 10% rather than 1% changes in relative humidity.

The humidity correction is least for the Burton-Pitt and greatest for the Limbrick, and there is a decided tendency for the correction to vary with the moisture content of the wheat. The significance of this has already been discussed.

Since a 10% change in the relative humidity of the test room has about the same, or less, effect than a 1° F. change in temperature, corrections are unnecessary if the relative humidity is within ±10% of that at which the calibration curve is applicable. The values given, however, may be useful for correcting calibration tables, etc., to the average relative humidity found in different localities, and if this is done it is doubtful if humidity corrections need to be applied at the time of making the test unless the humidity is extremely variable. The corrections given in Table X may be applied with assurance over the range 20% to 70% relative humidity at 72° F.

10. Summary of Conclusions by Sections

Design and Operation of Instruments (Section 2)

Only one of the meters tested, the Burton-Pitt, was of the dielectric type. This was found to be inferior to all the resistance type instruments studied, with the exception of the Davies. It is less stable, requires more adjustment, and is more affected by the temperature of the test room.

The Davies meter is not suitable for determining the moisture content of cereals. It is not sufficiently sensitive to give appreciable readings with grain of less than 16.0% moisture, and the galvanometer employed to measure the transmitted current is not capable of following the logarithmic resistance-moisture relationship over the range of moisture encountered. This necessitates frequent changes of voltage and the use of several calibration curves. The irregularity of the results and the large experimental error suggest that the design of the test cell is also faulty.

The Limbrick and Tag-Heppenstall instruments seem to be reasonably satisfactory in design, though the higher resistances measured in the Limbrick tend towards high humidity coefficients, and the metallized resistors are not of as stable a quality as the wire-wound type which can be used when the resistance to be measured is smaller. The large roller electrodes of the motor-operated Tag-Heppenstall meter proved to be superior to the smaller ones of the hand-operated model, feeding more uniformly and giving more consistent results, but both possess advantages over the static test cell.

Samples to be tested must be weighed for the Burton-Pitt, ground and measured to constant volume for the Limbrick, and packed in the test cell of the Davies. No preliminary preparation of sample is necessary for the Tag-Heppenstall meters. The Limbrick was found to be the slowest and the Tag-Heppenstalls the most rapid in operation, duplicate tests with the motor model of the latter requiring on the average only 1.2 minutes.

Neither the Burton-Pitt nor the motorized Tag-Heppenstall can be considered unconditionally portable instruments, for in addition to their bulk and weight, they require electrical power for operation.

Effect of Temperature and Humidity (Sections 4 and 5)

Results by all the meters studied were appreciably affected by temperature conditions, and also to some extent by the humidity. An increase in temperature increases the conductivity of the wheat. The temperature coefficient of the wheat alone was found to be appreciably different from the combined temperature coefficient of the wheat and Burton-Pitt or Limbrick tester. The temperature coefficient of the wheat–instrument system in terms of resistance or meter reading decreases with the moisture content of the grain in all the meters studied, but owing to the form of the calibration curve, when converted to a moisture basis it increases with moisture in the Burton-Pitt, decreases in the Limbrick, and is practically constant in the motor Tag-Heppenstall.

The effect of humidity also varies somewhat with the moisture content of the grain. It is most pronounced in the Limbrick, but in most cases a 10% change in relative humidity at 72° F. has less influence than a 1° F. change in temperature.

Calibration and Accuracy of Meters (Section 6)

A slightly curvilinear relation exists between the Burton-Pitt reading and the moisture content of wheat over the range 11.0 to 17.0%; at higher moisture contents this instrument gives erratic results. All the resistance type meters show a linear relation between moisture content and the logarithm of the resistance over the range 11.0 to 17.0% moisture. Above this point given increments of moisture cause a diminishing change in resistance, the relationship becomes parabolic, and the estimation of moisture progressively less precise, as shown by the experimental errors and the net standard errors of prediction given in Table XI. In all cases the "experimental error", as judged from the deviation of duplicate readings, represents only a fraction of the error of estimation of moisture content.

TABLE XI

Experimental error and net standard error of prediction of vacuum oven percentage moisture by electrical moisture meters

Meter	Experimental error (standard error of duplicates)		Net standard error of prediction	
	Moisture range 11.0 to 17%	Moisture range over 17%	Moisture range 11.0 to 17%	Moisture range over 17%
Burton-Pitt	0.06	0.10	0.54	—
Limbrick	0.08	0.09	0.38	0.49
Tag-Heppenstall (hand)	0.04	0.05	0.40	0.44
Tag-Heppenstall (motor)	0.02	0.03	0.16	0.56

Standard errors apply to mean of duplicates.

It is evident from Table XI that the meters fall in the following order of decreasing accuracy over the moisture range 11.0 to 17.0%, which is most important commercially: motor-operated Tag-Heppenstall, Limbrick, hand-operated Tag-Heppenstall and Burton-Pitt, the Davies being of no practical utility. Above 17.0% the Burton-Pitt gave quite erratic results. From a practical standpoint the Burton-Pitt is definitely inferior to the others, the Limbrick and the hand-operated Tag-Heppenstall about equal, and the motor-operated Tag-Heppenstall definitely the best over the lower, more important, moisture range, and only slightly, if at all, inferior to the Limbrick at higher moisture contents.

The moisture range of the different meters is not identical. The Burton-Pitt is capable of a wide range provided the sensitivity is changed. The Limbrick cannot be used to measure moisture contents lower than 11.5%, while 21.5% is the upper limit when set at the maximum sensitivity. This instrument can be adjusted to read grain of higher moisture content, but an additional calibration curve is then required. The lower limit of the hand-operated Tag-Heppenstall is about 9.0%, and that of the motor model about 7.0%. The upper limit of both is probably between 25 and 30%, but as with all the meters this is really determined by the increasing uncertainty of the result.

Effect of Grade and Variety of Wheat (Section 7)

Comparison of the limited number of low grade samples available with those of higher grade indicated that both high and low grade samples followed the same calibration curve in any particular meter, and there was no evidence of greater variability in the results obtained with the lower grades. Tests with Garnet indicated that in general it followed the same calibration curve as the other hard red spring wheat varieties represented in the general reliability series, in spite of the fact that the kernels of Garnet are harder. In the hand-operated Tag-Heppenstall meter however it showed a slightly higher resistance than expected. This seems to be due to inadequate roll spacing, and the accuracy of this instrument in general might be improved by using a wider spacing.

Acknowledgments

In addition to the individuals mentioned in the first paper of this series, the authors wish to acknowledge the assistance of Mr. D. S. Binnington and Mr. L. Sair, Research Assistants, Associate Committee on Grain Research, National Research Council of Canada, who were responsible for all of the meter determinations; special thanks are due to the former, who took charge of certain phases of the experimental work. They are also indebted to Mr. A. J. Grant, Physicist, National Research Laboratories, who measured the resistances and examined all the instruments before and after the investigation. Dr. J. T. Henderson, Physicist, National Research Laboratories, determined the temperature coefficient of several types of resistors.

The authors desire also to express their appreciation of the cordial co-operation of the individuals and firms who supplied the moisture meters for these tests, namely: the Davies meter, A. Gallenkamp and Co. Ltd., London; the Limbrick tester, Keyes Supply Co. Ltd., Ottawa; the Tag-Heppenstall hand- and motor-operated meters, C. J. Tagliabue Mfg. Co., Brooklyn, N.Y. The Burton-Pitt meter used was the property of the National Research Council of Canada, but Professor Burton kindly contributed suggestions with regard to its operation.

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ON A METHOD FOR MEASURING THE RESISTANCE OF VEGETAL TISSUES[1]

By Henri Prat[2]

Abstract

A method is described whereby numerical evaluations are introduced in the study of properties which in the past have been expressed qualitatively, namely, mechanical resistance and stages of maturation of vegetal tissues.

The building and operation of the apparatus are described. The results obtained in the case of growing and adult cereal straws are given. These reveal some important features in the mechanical construction of the culms of grasses.

Introduction

In the field of experimental plant morphology many data are qualitative rather than quantitative. For instance, stages of maturation of growing tissues, consistency of different tissues of a stem, etc., are usually described by force of circumstance in the general terms of "more" or "less" resistant without the possibility of giving numerical values to these terms.

Furthermore, in comparing different specimens, the difficulty is still greater. With these considerations in mind, this work was undertaken, in the hope of developing a method which would give more precise information in units that would allow of inter-comparisons being made between the various observations, at least within the limits of one set of experiments.

Apparatus

The first apparatus employed consisted of plain Roberval scales transformed by the addition of a cutting blade and a platform moved by a system of levers. Measurements of cutting strength obtained by adding weights to the apparatus proved unsatisfactory, the method being slow and imperfect, and it was soon realized that this quantity could be quickly and accurately read only from a direct-reading scale, using either a spring (dynamometer) or a gravity system.

The pressure applied to the blade used to cut the stem must be easily controllable and must be applied in such a way that there are no sudden irregular increases in the pressure. The apparatus shown in Fig. 1 proved satisfactory. The blade is moved by means of the rack and pinion of a microscope, M, a rod holding a frame for the interchangeable blade, B, being attached in place of the objective.

The cutting blade may be that of any scalpel or razor, but ordinary safety razor blades are most satisfactory, for such blades, when worn out, can be easily replaced by strictly equivalent ones. Dr. A. Navez has made careful observations on commercial safety razor blades and has shown that their sharpness, mechanically obtained, is adequately standardized and constant.

[1] *Manuscript received May 15, 1934.*
Contribution from the Department of Biology, University of Montreal, Montreal, Canada.
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Fig. 1 shows the general features of the apparatus equipped with a spring scale, as constructed in our laboratory at the University of Montreal. Fig. 2 shows the same apparatus fitted with a gravity scale. Such scales are preferable to spring scales, as their indications are more regular and progressive during application of the pressure.

The piece of tissue to be studied, for example a cereal culm, is fixed by some kind of strip to a narrow piece of wood, W, placed on the scale platform. It

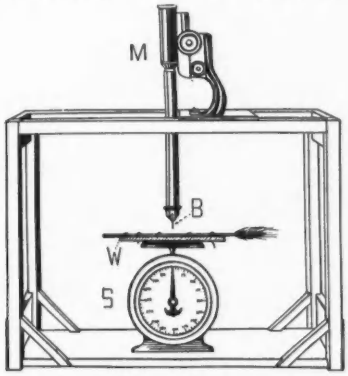

FIG. 1. *Outline of the apparatus equipped with a spring scale, S. M is the body of a microscope, B a movable blade, W a piece of wood supporting the stem.*

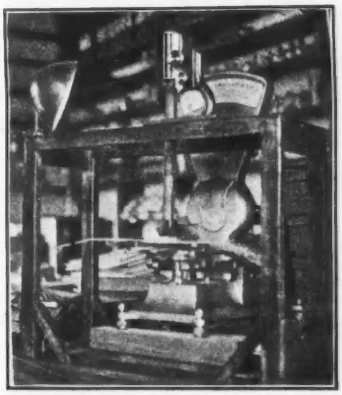

FIG. 2. *The apparatus equipped with a gravity-operated scale.*

is advisable to interpose between the stem and the wood several ribbons of bristol paper of appropriate width, to prevent the blade from touching the support before complete section of the tissue.

The moment of complete section of the culm can be detected by means of an electrical contact controlling a light or sound signal, but in general this improvement is not essential and the slight noise, shock, and jump of the piece is sufficient indication of completion of cutting.

The writer's experiments being performed with the intention of obtaining numerical data, as part of a general study of the growth of stems, and not for themselves alone, it was only after the completion of the experiments that the extent of the work of others along similar lines was realized. In this connection one may cite Albrecht (1), Holdefleiss (4) and Salmon (7). The property tested by these workers was *breaking strength*, measured by the application of pressure at right angles to the axis of a straw set up as a bridge between two supports. The quantity measured is thus practically "resistance to lodging."

The apparatus described in this present paper, devised to measure cutting and crushing strengths is however easily adaptable for the measurement of breaking strength. It is only necessary to place upon the platform a pair of supports upon which the straw rests (Fig. 4), and then to exert pressure

on the straw with the cylinder used in the determination of crushing strength. The writer intends to compare the breaking, crushing and cutting strengths of straws in a further publication.

Methods

Most of the stems examined were hollow cereal straws. If the hollow culm is placed entire on the testing platform, the measurement is often complicated by a preliminary crushing effect which occurs before cutting starts. For example, when the middle of an internode is sectioned, the following succession of phases is observed:—

(i) As progressively increasing pressure is applied, the stem is at first elastically compressed only, without permanent deformation (Fig. 3, A).

(ii) When the pressure reaches a certain value, the stem is crushed, and breaks into many narrow, distinct strips (Fig. 3, B).

(iii) After this crushing, the blade is working on a flat surface and for a time, as the pressure increases, the tissues are again in a state of elastic compression prior to actual penetration of the blade.

(iv) Finally the blade begins to section the peripheral sheath of sclerenchyma, then the vascular bundles and other tissues, and finally complete section is accomplished under a pressure easily read on the scale.

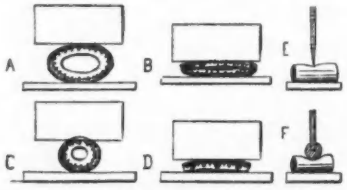

FIG. 3. *The cutting of a straw: A, elastic compression; B, crushing; C, sectioning of the solid portion of a straw, where cutting begins during the phase of elastic compression; D, cutting a split culm; E, measurement of cutting strength, with a blade; F, measurement of crushing strength, with a cylinder.*

It is necessary then, to consider two entirely distinct values, the crushing pressure and the cutting pressure. It is interesting to separate these two quantities as far as possible.

To this end, it should be noted that the cutting strength depends not only on the qualities of the straw but also on the sharpness of the blade used, while the crushing strength, for a linear contact, is almost independent of the characteristics of the blade, and may be considered as a definite property of each point of the straw.

With these facts in mind two complete series of measurements are performed on each sample; one with a razor blade (Fig. 3, E), the other with a metallic cylinder in place of the razor (Fig. 3, F).

When plotted, the data thus obtained produce two entirely different curves. In the middle of a hollow internode, the cutting strength is greater than the crushing strength. At the extremities, the central lacuna being locally reduced (Fig. 3, C), the crushing strength increases rapidly, while the cutting strength on the other hand decreases (Fig. 8). Close to the nodes, if a sufficiently sharp razor is used, section begins during the phase of elastic compression, and is completed before any permanent crushing occurs. When cutting is attempted in the middle of an internode, the unavoidable pre-

liminary crushing may introduce an error into the measurement of the cutting strength, in that, by reason of the shock incidental to crushing, actual cutting may be initiated at a lower pressure than would otherwise have been necessary.

It seems advisable to eliminate this effect by operating on half culms, obtained by longitudinal splitting (Fig. 3, D). The action of the blade is then very regular, reaching at the same time all parts of the material offered on a flat surface, instead of successively cutting parts of a round body as in case C, Fig. 3, or two identical sets of tissues placed one upon another as in B, Fig. 3. This procedure has the advantage also of allowing operation on strips of tissue of exactly known width.

To enable intercomparisons to be made between cutting strengths, experiments must be made with strips of equal width, *i.e.*, strips making contact with an equal length of the edge of the blade. If this precaution is not taken it is necessary to correct the readings in proportion to the widths of the strips used.

Measurements of width and thickness are made with a caliper provided with a vernier. Section should always be performed with the same face of the split straw facing the blade. This face should preferably be the outer one.

To increase the accuracy of measurement it is necessary to consider the rate of increase of the pressure. The cutting strength varies with different rates of application of pressure according to a complicated function of the sharpness of the blade and the qualities of the stem. It is necessary, therefore, to perform experiments under constant conditions if the readings are to be compared one with another. The time elapsing between the first contact and complete section of the stem must be as constant as possible, for example 20 sec., and during this time, pressure must be applied by a very regular and progressive motion of the focusing screw of the microscope.

Cutting strength may be defined as the maximum resistance offered to cutting by a standard blade moving under a steadily and slowly increasing pressure. It is measured in terms of the maximum pressure which can be applied to the blade without effecting complete section of the stem.

Under such conditions the fluctuations and values obtained may be less than 10 or 20%. This approximation is sufficiently accurate on account of the wide range of values obtained, *i.e.*, from 10 to 3000 gm.

The values given by such measurements cannot be taken as absolute numbers. They refer specifically to a given apparatus, with a given type of blade, and a given rate of application of the cutting force. With this reservation they are useful in giving numerical relations where formerly only qualitative data were obtainable.

Greater accuracy can be obtained by repeating measurements on neighboring points and closing each series of measurements by returning to the first point of observation. One thus eliminates errors due to any alteration in the characteristics of the blade which may occur during the progress of the work. Values obtained around the same level of the culm are averaged.

When observations must be made on neighboring points on the stems, it is especially useful to operate on split culms, otherwise crushing of the straw in the first experiment leaves the material in an altered condition for the next measurement. Before starting an experiment it is advisable to trace a metric scale on the internodes with India ink or glass-marking pencil. These guiding marks permit more rapid operation, as it is unnecessary to use a ruler to locate the points at which sections are to be made.

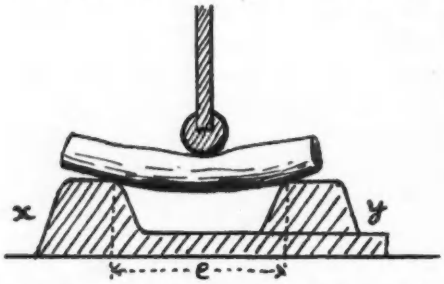

FIG. 4. *Adaptation of the apparatus for measuring breaking strength, x and y being supports which can be separated a variable distance, e, by means of a slide.*

The examples given below will show the application of the method.

Measurements

A. Young Culm

Consider first young culms with incompletely ripened tissues. Experiments may be performed under two conditions: (i) on the complete culm with the sheaths of the leaves wrapping the internodes, (ii) on bare internodes deprived of the leaves.

In the second case the resistance of a young culm is exceedingly low, particularly at the bases of the internodes. At these points the meristematic tissues of the growing zone are of an almost fluid consistency and the stiffness of the culm is due only to the rigidity of the sheathing leaves.

Fig. 5 shows resistances of a terminal internode of a flowering culm of a wheat (Blé Aurore), at the time of shedding of pollen (June 21, 1930). Measurements are relative to the bare internode and are taken on the whole straw without splitting.

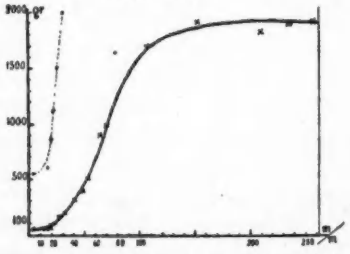

FIG. 5. *Resistance to section (cutting strength) of the terminal internode of wheat, at the time of anthesis (solid line). For clearness, the small values at the base of the internode are reproduced at the left (dotted curve), with the ordinates on a scale of 10:1 in comparison with the solid curve.*

Taking a sigmoid shape, the curve rises from 55 gm. at the base, to a value of 1900 gm. at about the middle of the internode. This value is maintained throughout the upper part of the internode. In the same sample of wheat, resistance of the axis of the ear is about 2000 gm. at the base, increasing a little (to 3400 gm.), and then decreasing gradually toward the apex (to 1100 gm.).

B. Growing Culm

Consider now a younger culm not yet fully grown. Fig. 6 shows a growing culm of rye *(Secale cereale);* on the left is a schematic diagram of the culm,

and on the right are graphs of the resistance of the tissues at points corresponding to those marked on the diagram. Measurements were taken directly, without splitting the culm, and without correcting the readings in proportion to the diameters. However, the range of values is so great (from 20 gm. to 2800 gm.), that these corrections are not necessary to an understanding of the structure of the stem

Resistances of bare internodes are indicated by crosses and solid lines. It will be noticed that the inferior internode E_2 offers a high resistance throughout its length (from 1600 to 2800 gm.). Maturation of tissues is here complete.

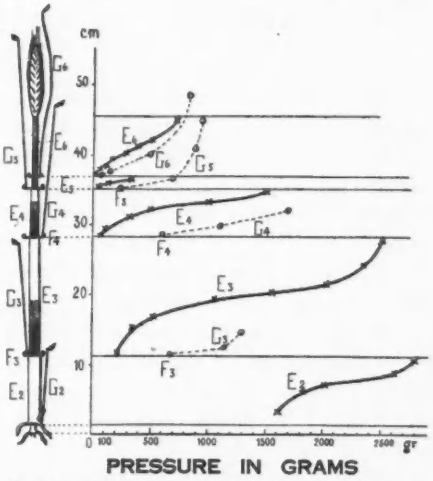

FIG. 6. *Experiments on a growing culm of rye: on the left, diagram of the culm; on the right, measurements of resistance (to section only) of the internodes at corresponding levels.*

The next internode E_3 is not entirely mature. In its upper part the resistance reaches 2500 gm., but at the base it is only 200 gm. This indicates the role played by the sheathing leaves in protecting the young stem. To show this still more clearly the resistances of the whole of each internode E with the sheathing leaf G, tested together, are indicated by circles joined by dotted lines (Fig. 6, G_3, G_4, etc.). It can be seen that $G_3 + E_3$ offers a resistance varying from 1100 to 1250 gm., instead of 200 gm. as offered by E_3 alone. The false node F_3 offers a low resistance (650 gm.), in full accord with its state of low differentiation. On the diagram on the left (Fig. 6) the parts of the internodes offering a resistance of less than 500 gm. are shown in black, those showing a resistance between 500 and 1000 gm., in cross-hatching, and those showing over 1000 gm., in white. Thus the superposition of very young meristems and consolidated tissues is clearly shown.

Internode E_4 offers in general a low resistance (under 1000 gm.). The highest value is 1500 gm. and the lowest 70 gm.

Internode E_5 is still younger and weaker; its resistance is 45 gm. at the base and 150 gm. at the top. It is entirely meristematic, but in compensation it is supported not only by its own leaf G_5 but also by the upper part of G_4.

Terminal internode E_6 is somewhat elongated basally: 85 mm. as against 15 mm. for E_5. In its lower part it is the weakest of all the internodes, its resistance being about 20 gm. at this point. It should be noticed however, that in its upper part, it is actually stronger than E_5, as it offers a resistance of 750 gm. This observation confirms the conclusions of Blaringhem (3)

and Athanassof (2), based on anatomical studies, that maturation occurs sooner in two regions: first in the base of the culm, then in the part immediately below the ear, leaving the intermediate internodes, such as E_5, in an inferior stage of meristematic development.

It can be seen from Fig. 6 that the terminal internode presents the maximum length of weak tissues. Along 5 cm. of its length it offers less than 500 gm. resistance, and on the other 3.5 cm., less than 1000 gm. Since the diameter here is also minimum (1.5 to 2 mm. as compared with 4 mm. for internode E_3), it is obvious that the terminal internode is, at this stage, particularly weak. However it is also the most protected of all the internodes, for sheaths G_6, G_5, and G_4 are wrapped around it and maintain it erect. Curve G_6 shows the necessity of this multiple "wrapping." Even the complex of $G_6 + E_6$ offers at the base a resistance of 150 gm. only, and only 50 gm. at the false node. If however one considers in addition the sheath G_5, a total resistance of from 700 to 900 gm. is obtained (Fig. 6, G_5).

It is a general rule in the growth of grasses that tissues are not exposed to the light and open air until they have reached a high degree of maturation. Before this time they are covered by previously matured organs. The basal position of the growing zones of leaves and internodes is essential if the above condition is to be maintained.

In Fig. 6 it will be noticed that if the centre points of the sigmoid curves showing resistances of internodes are joined, an approximately straight line, reaching zero at the base of the ear, is obtained (E_6 being excepted). This fact shows an element of regularity which characterizes the culm both in the dynamic and static state (5).

As regards the accessory conditions affecting the measurements, hydration of tissues must be considered in any study of young culms, particularly during the period of growth. Fortunately, parts of the culm most susceptible to desiccation are also the best protected by "wrapping", so that a fresh culm may be studied many hours after collection with the assurance that its characteristics remain unaltered.

In studies on mature culms, necessarily dried, all exigencies of this type are entirely eliminated, and experiments may be performed at any time after collecting, providing the temperature and relative humidity remain constant during the whole series of measurements on which inter-comparisons are to be based.

C. Mature Culms

When elongation of the internodes is completed and the ear ripened, the tissues of the culm also reach maturity. The lower parts of the internodes become rigid, and finally the terminal internode reaches a condition represented by the graph (Fig. 7). The middle part is the most resistant to section (see also Fig. 8, curve A,I) and, from this maximum, the values decrease regularly toward the extremity, if the terminal reinforcement already discussed is neglected. The upper and lower ends often have about the same resistance, frequently only one-half or even one-third that of the middle part.

The crushing curve (Fig. 8, A,II) is, in general shape, the reverse of the cutting curve; its concavity is upwards and the maximum values are reached toward the extremities, particularly the upper one. While the resistance is only 250 gm. in the lower part, and 500 gm. in the upper part of the hollow region, it increases to over 2000 gm. at the top of the internode. At the extreme base the crushing strength increases to only 700 gm. for the bare internode near the nodal diaphragm, but it reaches over 2000 gm. when the measurement is taken at the level of the coarse, dried, false node, with the wrapping leaf included.

All these observations can be related to the flexion and compression stresses borne by the different regions of the internode, and to the varying thicknesses of their walls. In the adult stage the mechanical role of the sheaths becomes of less and less importance, and when it comes to the time of harvest, the internodes are stiff enough to remain erect without the help of the decayed and dried leaves.

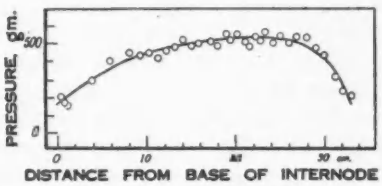

FIG. 7. *Resistance to section of an adult terminal internode of wheat. Apex to the right.*

Below the terminal one, the internodes are more resistant in direct relation to the greater stresses they must bear (Fig. 8, B). However in the basal part, resistance again decreases. Minima for section strength are reached at the extremities of the whole culm, even as they are reached at the extremities of the terminal internode alone. Of course mechanical stresses are similar whether one considers a whole culm or an isolated internode. The structure of the whole adult culm, from the point of view of anatomy, will be examined in detail in another publication.

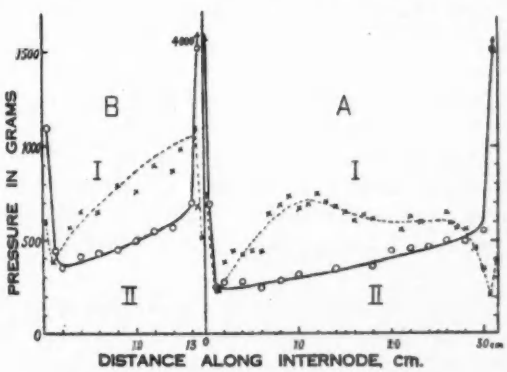

FIG. 8. *Cutting and crushing strengths of the terminal and subterminal internodes of a secondary culm of George Guthrie wheat (Central Experimental Farm, Ottawa): (I) graphs of cutting strength; (II) graphs of crushing strength; A, terminal internode; B, subterminal internode. All measurements on the bare internodes, with the apex to the right.*

To obtain measurements comparable from strain to strain* it is necessary to operate only on principal culms grown under the same conditions, and to take averages of many readings. Diameters, lengths of internodes, and the thicknesses of their walls must be measured at the same time. It is necessary also to eliminate

**Biological strains, i.e. varieties, etc.*

all imperfect culms, for any defect (injuries, insect galls, etc.) results in considerable changes in the mechanical properties of the tissues, generally by hardening them to a considerable extent.

A comparison of resistances to cutting and crushing is useful in a study of the probability of lodging in different varieties. As a matter of fact, however, factors other than mere resistance to a crushing or shearing stress affect lodging, in particular resistance to flexion and traction, and further work will have to be done on these matters before a complete understanding of the problem of lodging is obtained. These questions are not easy to investigate by reason of the difficulty of holding the tissues without injury, and also because of the practical impossibility of obtaining measurements at well determined and closely neighboring points. Thus, so far, determinations of cutting strength are superior to any other method in giving data more or less directly linked with other aspects of resistance.

In a practical application of the methods described above, the apparatus could be greatly improved by being rendered more or less automatic, and possibly self-recording, so that readings could be quickly and easily obtained from centimetre to centimetre along the length of a culm. This improvement would have the great advantage of eliminating the personal equation to a very great extent. Pressure would be applied very uniformly, section being determined by electrical contact between the blade and the platform. Such an installation would be more suited to an agricultural office than to a laboratory.

Summary

A simple method of measuring shearing (cutting) resistance of vegetal tissues has been described. Application of the method to cereal straws leads to the following conclusions.

The values obtained are obviously a function of several interrelated factors which will be separately investigated by other methods (histological, anatomical, physiological, etc.).

The method is useful, (i) in a study of the maturation of tissues in a growing stem, (ii) in comparisons of the characteristics of stems of different strains grown under similar conditions, (iii) in comparisons of the changes effected in the characteristics of stems of the same strain grown under different conditions.

It thus affords a means of analyzing the process of growth of a stem, the mode of protection of the young tissues (wrapping and unwrapping of the culm), and also of separating the effects of heredity from those of environment, as far as the question of the mechanical properties of the stem is concerned.

Acknowledgments

The writer is greatly indebted to Dr. Navez, of Harvard University, who has kindly read the manuscript, and to Dr. J. G. Fraser who provided specimens of cereals from the Central Experimental Farm at Ottawa.

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STUDIES ON THE DEHULLING OF BARLEY KERNELS WITH SULPHURIC ACID AND ON THE INHERITANCE OF REACTION TO COVERED SMUT *USTILAGO HORDEI* (Pers.) K. & S. INFECTION IN CROSSES BETWEEN GLABRON AND TREBI BARLEYS[1]

By W. H. Johnston[2]

Abstract

The use of concentrated sulphuric acid for dehulling seeds of barley hybrids in order to induce infection by *Ustilago hordei* (Pers.) K. & S., involved complications which made exact analysis of the reaction of the hybrids impossible. Although the hull showed a high degree of resistance to decomposition by the acid and appeared to afford the embryo sufficient protection against acid injury, there were wide fluctuations in degree of emergence of plants from treated seeds, both of hybrid and parent material. Much of the mortality among treated seeds was due to mechanical injury incurred before treatment. There was considerable seedling injury from infection by *Penicillium* spp. This was probably augmented by unfavorable germinating conditions. Increased severity of infection by *U. hordei*, due to the removal of the hull resulted in extreme distortion of seedlings and consequent failure to emerge.

Genetic studies were made on the F_2 of reciprocal crosses of Glabron, highly resistant, and Trebi, moderately resistant to the form of pathogen used. Infection percentages exhibited by the parents were regained in some F_3 lines and the hybrids showed little tendency towards greater susceptibility than the parents. Segregation for reaction to covered smut was not sufficiently clear to establish the inheritance of this character.

Slight correlation was demonstrated between smut reaction and height of plant, but none between smut reaction and barbing of awns or earliness of heading. The development of strains combining earliness, smooth awns, and resistance to covered smut should present no great difficulty.

Introduction

According to reports on the "Prevalence of Plant Diseases in the Dominion of Canada" for the years 1927–33 (4, 5, 15), covered smut is probably the most widespread and destructive disease of the barley crop occurring in western Canada. In the province of Alberta for the five-year period 1927–31, this disease is designated as being common, destructive and causing important losses. The report of 1931 (4) shows 50% of the fields examined to have been infected, one exhibiting as high as 70% infection. Covered smut was present in 33% of the fields examined in both 1932 and 1933 (4).

Little or no work has been reported concerning the breeding of improved varieties of barley, resistant to covered smut. The early development of seed treatment measures for the control of the disease may account in part for the lack of investigation in this regard. Possibly more important has been the lack of a satisfactory inoculation technique for obtaining successful infections. Investigators have reported unsatisfactory infections from

[1] *Manuscript received June 11, 1934.*
Contribution from the Department of Field Crops, University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada. This paper was constructed from a thesis presented to the Committee on Graduate Studies, University of Alberta, in partial fulfilment of the requirements for the degree of Master of Science.

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inoculating hulled* kernels (1, 2, 17). Dehulling by hand is impracticable when large populations are involved. The use of chemicals to dehull the kernels is still in the experimental stage and offers many difficulties.

The work reported in this paper summarizes the results of one phase of a general investigation conducted by the Department of Field Crops at the University of Alberta, Edmonton, during the years 1930–33. This general project had as its purpose the development of new, agronomically desirable, disease-resistant, smooth-awned varieties of barley, adapted to Alberta conditions (14).

Review of Literature

Environmental Considerations

The principal work regarding the effects of environment on the development of the covered smut disease in the barley plant is that of Faris (6, 7). Using controlled conditions, he was able to obtain high infection percentages of Hannchen barley over wide ranges of soil temperatures and acidity, and under moisture conditions generally existing in the soil at the time of seeding. Soil temperatures varying from 10–25° C. with 40–50% moisture content gave good infections at pH values of 5, 6, 7 and 7.8. In general, infection was inhibited by low soil temperature and moisture at time of seeding. Acid soils with 40 and 50% moisture content gave higher infections than did slightly alkaline soils. The vigor of the host plant was found to have little or no effect on the development of covered smut, although the growth conditions following infection may have a marked effect in that regard. The character of the soil was also found to play an important role in determining infection severity; quartz or builder's sand gave poor results while neutral potting soil gave normal infection.

Taylor and Zehner (18) have pointed out in the case of winter barley that higher percentages of infection with covered smut resulted from deep, than from shallow seeding.

Physiologic Specialization

Faris (6, 7) emphasized the fact that one of the important requirements necessary for high infection of covered smut in Hannchen barley was the use of inoculum collected from that variety. In a later paper (7), he demonstrated the presence of five physiologic forms by using four varieties of barley as differentials.

In covered smut collections obtained from Italy and several areas in the United States, Rodenhiser (17) distinguished seven physiologic forms on the basis of cultural characters. Two of these, a form obtained from Italy and one obtained from Minnesota, could also be distinguished by their pathogenicity on the varieties Lion and Himalaya.

Dehulling Studies

Tisdale (19) reported in the case of winter barley that the removal of the hull resulted in greatly increased infections. He removed the hulls by means

* *Throughout this paper the current practice is being followed of referring to "hulled" kernels, or varieties, as normal grain with the hull intact, and "dehulled" as kernels of hulled varieties from which the hulls have been removed artificially.*

of a scalpel and concluded that some simpler method of removing the hulls was necessary if extensive smut tests were to be carried out. Faris (7) also obtained greater infections when he used inoculated dehulled seed, but found that greatly reduced stands resulted.

Briggs (2) reported the results of extensive tests carried out at Davis, California, in the years 1919–21, with hulled seed of some 570 varieties and strains. Although the seeds were heavily inoculated with viable spores little infection resulted. Barley covered smut tests carried out at the University of Alberta in 1931 (1), with hulled kernels, confirmed the results reported by Briggs.

To obtain some simple method of dehulling the barley kernel, Briggs (2) studied the possibility of using sulphuric acid. It had been previously demonstrated by Brown (3) that the seed coat of barley was surprisingly resistant to this chemical. Briggs in his investigations varied both acid concentration and duration of treatment, but came to no definite conclusions regarding the most suitable treatment. Fortunately the hull over the germ was found to be thicker than elsewhere on the kernel, and a thin covering often remained over this region when the remainder of the kernel was completely dehulled. There appeared to be considerable variations in smut infection after apparently equal degrees of dehulling, due probably to the small numbers of plants used. He also found that low concentrations of acid for a long period of time gave infections comparable to high concentrations for short periods of time. A certain amount of corrosion of the kernels was noted when the more concentrated acid was used. It was also observed that complete dehulling was not necessary for good infection; in fact, a thin hull over the entire kernel seemed to give optimum results. He concluded that seed treated with sulphuric acid gave results comparing very favorably with seed dehulled by hand, and gave promise of usefulness in testing hybrid populations for smut reaction.

Experimental Studies

Materials and Methods

All genetic studies reported in this paper were carried out with reciprocal crosses between the varieties Trebi and Glabron. Trebi is a six-rowed, rough-awned variety resulting from a pure line selection from an importation, S.P.I. No. 15821, made in 1907 in the co-operative breeding experiments conducted by the United States Department of Agriculture and the Minnesota Agricultural Experiment Station at St. Paul, Minnesota (10).

Glabron is a six-rowed, smooth-awned variety, developed at the Minnesota Agricultural Experiment Station from a back-cross between Smooth-Awn (a selection from a cross between Lion × Manchuria) and Manchuria (11).

Trebi is moderately susceptible to infection with *U. hordei* in tests carried out at the University of Alberta, whereas Glabron is highly resistant (1).

The F_3 generation was used in all genetic studies reported, the purpose being to classify the F_2 plants on the basis of the infection percentages of the F_3 lines. Approximately 50 seeds were sown per 10-ft. row. Parental varieties were included at intervals of approximately 30 rows. The smut reactions of approximately 800 F_3 lines were tested.

The method of dehulling the kernels with sulphuric acid which was used in these studies will be described in detail later in this paper.

Inoculum consisting of a composite sample of chlamydospores collected from Velvet, Comfort and the two parent varieties was used in all inoculations. The method of inoculation consisted in shaking, in an envelope, a liberal quantity of the spores together with the dehulled seeds. In all cases the viability of the inoculum was tested before use by germinating the spores in water cultures.

The inoculated dehulled kernels were sown in a neutral soil with a temperature approximately 16° C. Owing to the dry condition of the soil it was necessary to seed two to two and a half inches deep instead of one to one and a half inches, the usual depth.

Dehulling with Concentrated Sulphuric Acid

Laboratory and field results.—To facilitate the dehulling of the barley kernels, a method of removing the hull with sulphuric acid was decided upon. Since no conclusive evidence as to the optimum strength and duration of treatment could be drawn from previous investigations, it seemed advisable to conduct a special study in an attempt to obtain further information on this problem.

To make possible the treatment of several samples of barley at one time, the apparatus shown in Fig. 1 was devised. This apparatus consisted of a tray composed of a wooden frame coated with paraffin, and four strands of copper wire serving as a support for two rows of fine bronze netted-wire baskets. The identity of the latter was kept by numbers inscribed on the frame. The method utilized in dehulling the kernels of the parental varieties will serve to illustrate the general technique adopted, while a modified method, used in dehulling the kernels of the F_2 hybrid plants, will be described later.

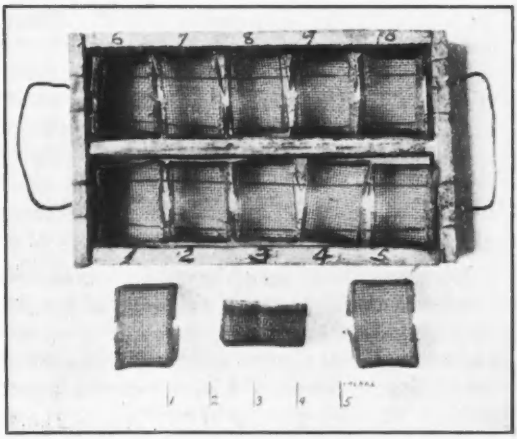

FIG. 1. *Immersion tray (including wire baskets) used in dehulling barley kernels with sulphuric acid.*

The tray containing the ten samples was immersed in the concentrated acid for a period of approximately five minutes, then removed and plunged quickly into cold water, in which the kernel lots were washed vigorously for about two minutes. To neutralize any acid that might still remain on the kernels the tray was next immersed in a concentrated solution of baking soda ($NaHCO_3$) for a period of two to three minutes. The kernels were then washed a second time in water before being placed on blotting paper to dry.

This treatment dehulled the majority of the kernels of the parent varieties fairly completely. A moderately thick hull remained over the embryo, whereas the amount of hull persisting over the remainder of the kernel varied from 25–50%. The kernels of Trebi appeared on the whole to have thicker or more resistant hulls than those of Glabron.

During the operation described above, it was discovered that if the kernels which had been treated for two to three minutes were washed in water and replaced in the acid for a few seconds when still wet, rapid and complete dehulling took place. That is to say, with the exception of the embryo region, over which a thin hull remained, the kernel was rendered more or less free of hull. This procedure appeared so promising in the light of laboratory germination tests, that it was decided to utilize it in dehulling the kernels of the F_2 plants. The technique employed in this modified treatment differed from that described above only in that the kernel lots were removed from the acid after a duration of two minutes, washed in cold water and replaced in the acid for the brief period of ten seconds. Some 50 to 60 lots of kernels could be treated and washed in an hour by this method.

Criticism may be made of this phase of the work, in that different methods were used in dehulling the hybrid and parental materials. Briggs (2) has pointed out that complete dehulling of the kernels is not necessary for optimum infection. With this in mind, it may be concluded that slight variations in the degree of dehulling will have little or no effect on the percentage of smut finally appearing in the plants produced from such kernels. Furthermore, it will be seen later in the paper that no observable differences in germination existed between the parental and hybrid lots of treated kernels. For these reasons, and to avoid confusion, no distinction will be made, in the remainder of this paper, between these two methods of dehulling barley kernels.

Examination of treated lots of kernels of both parental and hybrid material showed that the degree of dehulling of the kernels of individual plants was very uniform. The only kernels exhibiting variation were those whose hulls had been injured prior to treatment. On the other hand, observations on the variability in degree of dehulling amongst the kernel lots of different plants showed that, whereas no differences were apparent between the parental replicates, striking differences prevailed between kernel lots of different F_2 hybrid plants. The kernels of some plants showed an extreme condition of dehulling, while others showed a more moderate type, similar to that of the parents. These results indicate that the F_2 hybrids were segregating for thickness of hull or resistance to decomposition by acid.

It has been already pointed out that the dehulled kernels were sown in a comparatively dry soil. This condition was aggravated by the fact that no rain fell for a period of seven or eight days following seeding. That these factors checked normal germination was shown by the rapid and increased emergence which occurred after the first rain following seeding. Nevertheless, the final emergence of both hybrid and parental lines was disappointing. Large fluctuations occurred throughout the nursery. As the 50 kernels seeded per row were only estimated, it is impossible to state with accuracy the average reduction in stand of lines resulting from treated inoculated seed. However, a comparison of the stands resulting from treated seed with those resulting from untreated seed may be of interest. It was found that 65% of the hybrid lines, and 71 and 39% respectively of the Trebi and Glabron rows resulting from acid-dehulled seed, contained less than 25 plants. On the other hand, only 5% of 150 random hybrid lines (approximately 50 kernels per line) grown from normal hulled seed, contained less than 25 plants. Similar study of 50 random rows of each parent showed that only 4% of the Trebi rows and 2% of the Glabron rows had stands of plants below this limit.

Although the kernels of Trebi showed a greater thickness of hull than those of Glabron after acid treatment, it is interesting to note that the latter showed considerably less seedling loss. If any relationship existed between the degree of hull remaining on the kernel after acid treatment, and ability to emerge under field conditions, it was evidently masked by the activity of other agencies. The poor emergence of Trebi as compared with that of Glabron is thought to be due either to the characteristically slower germination of the kernels of the former, which would predispose them to attack from blue mold or other agencies, or to the greater susceptibility of this variety to the covered smut pathogen. It was expected that, since the kernel lots of the parent varieties showed a greater uniformity of dehulling than those of the hybrid lots, they would also show a correspondingly greater uniformity of field germination. The equally erratic germination of the hybrid and parental lines again leads to the belief that factors other than the degree of decomposition of the hull are responsible for the lack of field emergence noted.

Factors involved in seedling injury. An examination of the lines showing reduced stands revealed the fact that in a large number of cases germination had commenced, but owing to either the direct weakening effect of the acid or the indirect effect of dehulling, which exposed the young seedlings to a number of adverse environmental factors, the seedlings were unable to reach the soil surface. This inability to emerge was often accompanied by a condition of extreme distortion (Fig. 2, *B*). Faris (6) observed a similar distortion and lack of emergence of barley seedlings grown from hand-dehulled, inoculated seed. It seems reasonable to suppose that the removal of the hull unduly exposes the young seedlings during the early germination period, at a time when they are particularly susceptible to injury.

Other seedlings were found whose growth processes were early arrested by attack from blue mold fungi, *Penicillium* spp. (Fig. 2, *C*). The development of the root system seemed but slightly impaired, the greater injury occurring to the plumule. The stage of germination at which infection occurred varied widely, some seedlings being attacked just as the plumule was emerging through the coleoptile, others escaping until the plumule was well emerged.

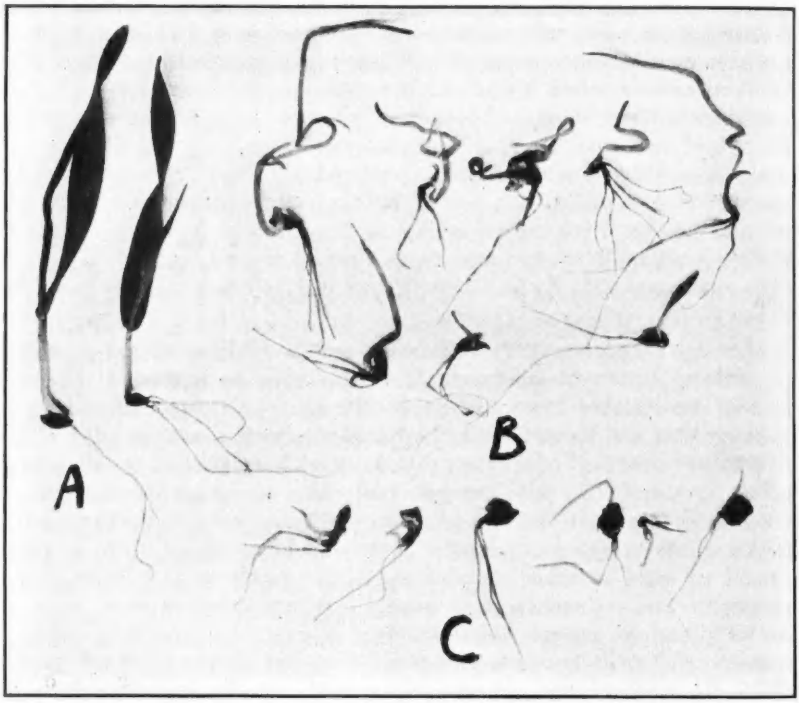

FIG. 2. *Injury to barley seedlings grown from kernels dehulled by sulphuric acid followed by inoculation with chlamydospores of Ustilago hordei. A. Healthy seedlings from non-dehulled uninoculated seed; B. Distorted seedlings from dehulled inoculated seed; C. Seedlings from seeds treated identically with B, showing distortion and stunting as a result of attack by mold fungi shortly after germination.*

Kernels showing no sign of germination were found in all the rows examined. This lack of vitality will be shown later to be due generally to seed coat injuries received prior to acid treatment.

In an endeavor to throw some additional light on the question of what factors were influential in reducing seedling emergence, two experiments were conducted in the greenhouse. Owing to the relatively small number of kernels used, certain minor variations between varieties occur; consequently only averages will indicate reliable trends.

Experiment I was conducted for the purpose of determining whether or not a higher activity on the part of the pathogen *U. hordei* could explain the

distortion of seedlings resulting from inoculated dehulled seeds. For this purpose uninoculated and inoculated lots of normal, hand-dehulled and acid-dehulled seeds of five varieties of barley were sown in sterilized soil. Fifty kernels, inoculated with a composite sample of smut spores, were used in each treatment. The temperature prevailing during this experiment was approximately 15° C. The results obtained are shown in Table I.

TABLE I

PER CENT SEEDLING EMERGENCE OF FIVE VARIETIES OF BARLEY, HULLED, DEHULLED BY HAND, AND WITH SULPHURIC ACID, WHEN INOCULATED WITH SPORES OF *Ustilago hordei*

Variety	Number*	Per cent emergence					
		Normal hulled		Dehulled by hand		Dehulled by acid	
		Uninoculated	Inoculated	Uninoculated	Inoculated	Uninoculated	Inoculated
Bearer	C.A.N. 704	90.0	90.0	100.0	80.0	60.0	53.3
Glabron	C.A.N. 718	93.3	80.0	90.0	76.7	50.0	40.0
O.A.C. No. 21	C.A.N. 734	93.3	96.7	66.7	46.7	33.3	23.3
Saskatchewan Sel.	N.S.N. I-25-5	86.7	80.0	96.7	63.3	30.0	20.0
Trebi	C.A.N. 753	86.7	86.7	83.3	80.0	43.3	33.3
Average of the five varieties		90.0	86.7	87.3	69.3	43.3	34.0

* *C.A.N.—Canadian Accession Number.*
N.S.N.—Nursery Stock Number, University of Alberta.

The considerably lower germination percentage exhibited by the acid-dehulled seed, is again attributed to mechanical seed coat injuries received before acid treatment. The significance of this form of injury will become more apparent after considering the data contained in Table II. It will be noted also that, whereas there is little if any difference in the percentage emergence of uninoculated and inoculated hulled kernels, there is considerable difference in this regard in the dehulled series. The inoculated lots of kernels are invariably lower in emergence percentage. Examination of the soil supporting the inoculated lots revealed the presence of distorted seedlings. The results obtained here are especially significant in the case of hand-dehulled seed, and support the view that seedlings are injured by infection with *U. hordei*. An attempt to carry a number of the inoculated seedlings to maturity proved futile, as the conditions existing in the greenhouse were not conducive to normal heading. The spikes were small and in most cases sterile. Only two spikes exhibiting smutted spikelets were found. In view of the facts that viable inoculum was used, and that the temperature prevailing during the experiment was favorable, it can be safely assumed that considerable seedling infection actually did take place.

Experiment II was outlined to obtain some definite data on the ability of kernels, injured as a result of threshing operations, to germinate and emerge after acid treatment. Four varieties of barley were used in this experiment. Two lots of 50 seeds were made up from each variety, a random sample and one containing only those kernels showing some break of the hull over the embryo. It is important to point out that the latter sample contained no kernels with the embryo fully exposed. The results, as summarized in Table II, give ample evidence of the complete inability of kernels possessing mechanically damaged hulls to germinate after acid treatment.

TABLE II

PER CENT EMERGENCE OF SEEDLINGS FROM NORMAL AND MECHANICALLY INJURED KERNELS OF FOUR VARIETIES OF BARLEY AFTER TREATMENT WITH SULPHURIC ACID

Variety	Number*	Per cent emergence			
		Normal		Injured	
		Non-treated	Treated	Non-treated	Treated
Canadian Thorpe	C.A.N. 816	93	43	83	0
O.A.C. No. 21	C.A.N. 734	93	63	87	0
Saskatchewan Sel.	N.S.N. I-25-5	100	50	53	3
Wisconsin Barbless	C.A.N. 758	100	90	93	0
Average		97	62	79	1

* *C.A.N.—Canadian Accession Number.*
N.S.N.—Nursery Stock Number, University of Alberta.

Discussion

There was great variation in field germination of seed lots which received equal treatments with sulphuric acid. Precaution had been taken during the dehulling process to regulate the treatment so that a thin hull would remain over the germ of the kernels. Although minor variations in this regard were noted amongst the kernel lots of the hybrid lines, in no instances were seeds rendered entirely devoid of hull over this region. Furthermore, an examination of the embryos of kernels exhibiting the more extreme form of dehulling disclosed no noticeable injury. It appears, therefore, that under the conditions of this study, the hull of the barley kernel is quite resistant to digestion by sulphuric acid, and in the absence of complicating factors provides the embryo with ample protection. Studies now in progress (1) indicate that barley varieties differ considerably in thickness of hull or in resistance of the hull to acid decomposition. Trebi and Glabron were both found to belong to the group possessing the thicker or more resistant type of hull. This finding is in accord with the view expressed above.

A condition of the kernel that has been shown to be very effective in predisposing it to acid injury, is that resulting from seed-coat injuries over the germ, obtained as a result of threshing. The kernels used in the genetic

studies reported in this paper were threshed by a small head thresher. They were thought to be without extensive mechanical damage at the time of acid treatment, but subsequent and more careful scrutiny of other lots of kernels threshed by a similar method, showed the existence of numerous breaks of the hull over the embryo. Many of these were apparent to the naked eye, while others were observable only under a hand lens.

It is thought that these mechanical ruptures of the hull not only allowed the acid to come into contact with the embryo, but were instrumental in preventing complete removal of the excess chemical after treatment. It is conceivable that any delay in removing the acid might result in fatal injuries to the embryo. The low emergence percentages shown by the acid-dehulled kernels in Table I, are in all probability due to seed injuries received before acid treatment. The kernels in question were threshed by a rod-row thresher, which tended to leave the hulls in a greatly impaired condition. Here again the seriousness of these ruptures was not appreciated until after acid treatment.

Hurd (13) reports the presence of a natural rupture at the hilum end of the seed coats of threshed kernels of the Turkestan and Coast types of barley. This occurred whether the kernels were threshed by machine or by hand. Prolonged exposure of such kernels to saturated copper sulphate solution resulted in high mortality, whereas similar treatment of kernels left attached to pieces of the rachis resulted in no injury. She concluded that these fatalities occurred as a direct result of the chemical coming into contact with the embryo of the kernel by way of the natural rupture at the hilum. Since the spike structure of the two parental varieties used in this study appeared similar to that of the Coast variety, an experiment based on that of Hurd was conducted, to obtain data on the possibilities of sulphuric acid injury arising through the source just described. The duration of treatment in this experiment was identical with that used in dehulling the kernels of the hybrid lines. The results showed no difference whatsoever between the germination percentages of kernels treated while still attached to the rachis, and those treated in the threshed condition. This result is not surprising in view of the extremely limited exposure of the kernels to the acid. It may therefore be concluded that injury through the source reported by Hurd was not an important factor in reducing germination of the kernel lots used in the present investigation. However, it is significant that the mechanical seed coat injuries mentioned earlier in this section of the paper, arose from this natural rupture at the hilum. It is the existence of this weakness in the seed coat at the embryo end of the barley kernel that necessitates so much care in threshing kernels intended for chemical treatment.

The nature of the injury occurring from blue mold fungi was not apparent from field studies made. Hurd (13) has contributed valuable information in this regard in the course of a study on the susceptibility of injured wheat seeds to mold. Kernels with broken pericarps were germinated on blotters thickly sprinkled with spores of *Penicillium* spp. and *Rhizopus nigricans.*

She found that when the seed coat was ruptured over the endosperm 100% fatal infections occurred, whereas when the break occurred over the embryo the kernels proved immune. Also, injury from using copper sulphate and formalin as seed treatments, rendered previously immune seeds immediately susceptible, even perfect seed coats no longer acting as a protection. These observations of Hurd in regard to wheat would seem to explain admirably the nature of mold injury noted in this study. The acid treatment invariably exposed the endosperm at the distal end of the barley kernel, thus affording the mold fungus an excellent point of entrance. Furthermore, any injury of the embryo by acid would tend to render the kernel more susceptible.

It was felt that much less seedling injury from mold fungi would have occurred had conditions been more favorable for rapid germination. This supposition is supported by the evidence of Meyers (16) who found that mutilated corn seeds showed much less fatal injury from molds when conditions were favorable for germination.

Evidence also pointed to the fact that removal of the seed coat predisposed the young seedling to severe attack by the pathogen *U. hordei*. This was manifested in extreme distortion. A similar type of seedling injury has been reported by Tisdale and Tapke (20). These investigators, studying the possibilities of seedling infection as a result of inoculating hand-dehulled barley seed with spores of the loose smut fungus *Ustilago nuda*, showed definitely that the activity of the pathogen was responsible for distortion of seedlings noted in their work. They also found that dehulled inoculated seed sown three-fourths of an inch deep emerged more satisfactorily than similar seed sown one and one-half inches deep. Depth of seeding may also have been a complicating factor in the present study (see Materials and Methods).

Genetical

Inheritance studies. The reactions to the covered smut disease of the lines of nine crosses, involving Glabron and Trebi, were determined. Considerable variation in the severity of infection of individual plants was noted. This was due to the fact that the first spikes to emerge from the sheath tended to escape infection. Infected culms were found to be slower in heading than the healthy ones, and in a few cases the smutted spikes, rather than pushing their way through the top of the sheath, simply forced their way through the base. In one or two cases the peduncle bearing the smutted spike was badly distorted. In no instance did the leaves show smut sori as observed by Faris (6) in the case of severely infected plants.

All plants exhibiting any degree of infection were termed susceptible. Owing to reduced stands, the percentage infection was calculated for only those F_3 lines containing 15 or more plants. The lines were grouped in classes according to the percentage infection, in class intervals of 10%. A zero class was added to include all lines showing no infection.

The reaction of F_3 lines and parental varieties to the covered smut disease is given in Table III. The Glabron parent appeared highly resistant to the

collections of the pathogen used, and Trebi moderately so. The inherent resistance possessed by Glabron was really much greater than the data would indicate, as the majority of the rows contained only one partially infected plant. Parental rows of Trebi, on the other hand, often exhibited several totally infected plants. The overlapping of the ranges of infection percentages shown by the two parents, together with the wide range in this regard exhibited by Trebi, rendered impossible the working out of any definite mode of inheritance for covered smut reaction. Hybrid lines were found exhibiting the high degree of resistance of Glabron, while others showed susceptibility equal to that of Trebi. The resistance shown by the parental varieties was reflected generally in the progeny, there being little evidence of transgression towards greater susceptibility.

TABLE III

REACTION OF F_3 LINES AND PARENTAL VARIETIES TO INFECTION WITH *Ustilago hordei* IN RECIPROCAL CROSSES OF GLABRON AND TREBI

Parent or cross	No. of cross	Infection classes in percentage						
		0	1–10	11–20	21–30	31–40	41–50	51–60
Trebi	—	—	2	11	8	4	2	—
Glabron	—	9	24	2	—	—	—	—
Glabron × Trebi	6	2	14	10	6	1	1	—
	11	—	8	29	18	11	3	—
	12	13	49	37	10	6	3	2
	13	22	33	22	14	3	2	1
Trebi × Glabron	19	2	21	10	7	6	4	1
	20	4	11	24	10	8	4	1
	21	—	15	13	14	12	3	3
	23	—	6	11	17	10	9	1
	45	20	17	24	7	1	1	—
Total hybrid lines	—	63	174	180	103	58	30	9

Correlation studies. The importance of correlation studies in connection with the inheritance of disease reaction cannot be overestimated. This type of inheritance does not always lend itself readily to factorial analysis, and often it is only through establishing certain associations between the factors concerned in resistance and susceptibility, with those of some easily distinguishable morphological character, that it is possible to determine the number of factors concerned in a given disease reaction. Griffee (9) demonstrated in a striking manner the value of such linkage studies. He was able to show, by studying the reaction of F_3 lines to *Helminthosporium sativum* in relation to three other independently inherited characters, that at least three factors were concerned in resistance to this pathogen.

As part of the more general program alluded to earlier in this paper (14), data were compiled on the mean number of days from emergence to heading, as well as on the mean height of each F_3 line of the two crosses 12 and 21 (see Table III for parentage of crosses). Barbing of awn was also studied in these two crosses as well as in cross 45.

The results of these studies may be briefly summarized. Barbing of awns was found to be governed by two factor pairs which could be explained on the basis of epistasis. Rough, intermediate-smooth and smooth-awned plants were obtained in the ratio of 12 : 3 : 1 in the F_2. Earliness of heading was shown to be an inherited character and could best be explained by assuming two main complementary factors. Transgressive segregation for earliness and lateness occurred in both crosses studied. The coefficient of variability of the F_3 lines in regard to mean number of days from emergence to heading was 7.37 ± 0.27 and 7.55 ± 0.35 for crosses 12 and 21 respectively. The coefficient of variability of the parental varieties, on the other hand, ranged from 2.11 ± 0.45 to 3.56 ± 0.60. Height of plant was found to be readily influenced by environment. This was particularly evident in cross 21, in which the parents showed coefficients of variability of 7.00 ± 1.49 and 5.59 ± 1.19, as compared with the value 8.42 ± 0.39 shown by the hybrid lines. More positive evidence regarding the heritable nature of this character was obtained from cross 12. The F_3 lines of this cross showed a coefficient of variability of 7.74 ± 0.29, as compared with 4.88 ± 0.82 and 4.71 ± 0.79 of the parent varieties.

In order to determine whether any association existed between the different combinations of smut reaction, height of plant and number of days to heading, simple correlation coefficients were calculated (12). These values may be found in Table IV. High correlations exist between mean height of plant and mean number of days to heading. Smaller but significant positive correlations exist between covered smut reaction and both mean height of plant and mean number of days to heading in cross 21, as well as between smut reaction and height of plant in cross 12. The value $r = .193 \pm .059$ obtained between mean number of days to heading and covered smut reaction in cross 12 is of extremely doubtful significance. To determine the causal relationships existing between these variables, partial correlations were calculated (8). These data are also presented in Table IV.

TABLE IV

SIMPLE AND FIRST ORDER PARTIAL CORRELATIONS BETWEEN SMUT REACTION AND BOTH MEAN HEIGHT OF PLANT AND MEAN NUMBER OF DAYS FROM EMERGENCE TO HEADING

—	Number of cross	Simple correlation coefficients				First order partial coefficients
		Mean number of days to heading (2)		Per cent covered smut infection (3)		
Number of cross		12	21	12	21	
Mean height of plant (1)	12	.728 ± .025	—	.266 ± .060	—	$r_{12.3}$ cross 12 + .715 ± .026 cross 21 + .688 ± .034
	21	—	.737 ± .030	—	.498 ± .065	$r_{12.3}$ cross 12 + .187 ± .062 cross 21 + .362 ± .075
Mean number of days to heading (2)	12	—	—	.193 ± .059	—	$r_{23.1}$ cross 12 − .003 ± .061 cross 21 − .002 ± .086
	21	—	—	—	.366 ± .075	

The relationship between mean number of days to heading and mean height of plant appears to be little influenced by degree of smut reaction. On the other hand, when the variable mean height of plant is held constant, no association whatsoever exists between mean number of days to heading and degree of smut reaction. With mean number of days to heading held constant, a small but significant positive correlation is found between degree of smut reaction and mean height of plant in cross 21, and one of doubtful significance in cross 12. However, it is possible that limited genetic linkage exists between the factors concerned in smut resistance and those concerned in height of plant.

The correlation ratio (12) was employed to determine a possible relationship between barbing of awns and degree of smut reaction. The value, $\eta = .030 \pm .043$ obtained, is indicative of an entire lack of association between these characters.

Conclusions

An adequate and uniform population is essential for any genetic investigation. It is evident that the stands resulting from kernel lots dehulled with concentrated sulphuric acid, were too variable to be of great value in testing the reaction of a hybrid population to *U. hordei*. Evidence indicated that under the conditions of this study the hull of the barley kernel was quite resistant to the acid, and when free from mechanical injuries offered the embryo ample protection. A complex of factors was found responsible for the lack of field emergence noted in this study. Notable among these was the acid treatment of kernels possessing hulls broken in the embryonic region. After dehulling, increased pathogenic activity of the covered smut fungus, together with attack by blue mold fungi, resulted in a further toll of the young seedlings. Unfavorable germinating conditions were thought to have aggravated the general situation.

The reader should not be unmindful of the fact that only concentrated acid was used. Hence, a too hasty condemnation of the chemical would not be justified. However, under the conditions of this investigation, it is unlikely that a less concentrated form would have proved any more satisfactory; since, to obtain the same degree of dehulling, the kernels would necessarily have to be treated for a greater period of time. This would have afforded the acid even a greater opportunity of coming into contact with the embryo, had any rupture of the hull been present. However, it is possible that the degree of dehulling attained in the present study was more complete than was necessary for good infection. In that event a less concentrated solution of acid might have proved more satisfactory. It was felt, furthermore, that even the concentrated acid might have proved more or less successful had the precaution been taken to thresh all kernel lots by hand, so that the seed coats would be free of injury. Again, there is always the possibility that further research will bring to light chemicals more satisfactory for dehulling

barley kernels than sulphuric acid. At this juncture the question might well be asked; Is further investigation of the use of chemicals as dehulling agents warranted?

Surveys have shown the existence of comparatively high natural infections of covered smut in farmers' fields. These cannot always be attributed to superior environmental conditions in these fields, or to the presence of a more virulent form of the pathogen, since such factors have been readily controlled by investigators. The most plausible explanation would appear to lie in the practice of close threshing followed by many farmers, which tends to leave the barley kernels in a more or less dehulled state, descriptively termed "skinned". In this connection Faris (7) makes the following statement: "I have no doubt, however, that in farm practice, injury to the hull over the seed embryo may play a part in the amount of loss from this barley smut. In fact, I have received field-threshed barley with a considerable portion of the seed as effectively dehulled by close threshing as could be done by hand." The writer has also seen barley samples so badly "skinned" as to compare favorably with hand-dehulled seeds in the completeness of dehulling.

In the light of the above observations, it would appear that the development of some system of close threshing would possibly prove more fruitful as a means of inducing covered smut infection, than continued research with chemicals. Tisdale (19) has suggested that scarifying the seed before smutting might possibly give as good results as removing the hulls by hand. One obvious advantage of dehulling barley kernels in some way other than by chemicals, lies in the fact that machine-threshed seed could be safely used.

Doubtless, a certain percentage of seedling loss would still occur from seed mutilation and from the activity of other agencies discussed earlier in the paper. These losses could be readily offset by increasing the number of kernels sown per row.

Genetic studies reported in this paper, while failing to reveal any definite mode of inheritance of covered smut reaction, clearly demonstrate its heritable nature. Since no genetic linkages appear to exist between covered smut reaction and either earliness of heading or barbing of awns, no great difficulty should be experienced in developing new homozygous strains possessing the desired combination of earliness, smooth awn and smut resistance.

Acknowledgments

The writer wishes to make grateful acknowledgment to Dr. O. S. Aamodt, Professor of Genetics and Plant Breeding, University of Alberta, who suggested this investigation, supplied the materials and gave valuable assistance during the course of the study; to Mr. A. Platt for assistance in certain technical phases of the investigation; and to the National Research Council of Canada for financial assistance received.

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ON THE INVASION OF ROOTS OF *MEDICAGO* AND *MELILOTUS* BY *SCLEROTINIA* SP. AND *PLENODOMUS MELILOTI* D. AND S.[1]

By M. W. Cormack[2]

Abstract

The invasion of roots of *Medicago* and *Melilotus* by *Sclerotinia* sp. and *P. meliloti* was studied, with particular reference to the effectiveness of wound cork in arresting the progress of these pathogens. Both pathogens are apparently capable of penetrating through the uninjured external cork covering of the roots and also through any subsequently formed wound cork layers. Killing of the root tissues and retardation of wound cork development in advance of hyphal invasion was caused by both pathogens. No explanation can at present be offered as to why the advance of *P. meliloti* is checked and that of *Sclerotinia* sp. is definitely slower after good growth begins in the spring.

Recent studies of Sanford and Cormack (9, 10) have shown that *Sclerotinia* sp. and *Plenodomus meliloti* are destructive root-rotting pathogens of *Medicago* (alfalfa) and *Melilotus* (sweet clover) in Alberta, especially following the winter dormancy period. During the summer, *P. meliloti* ceases to be pathogenic, while *Sclerotinia* sp., although still capable of rotting the roots, causes far less damage than it does in the early spring. It was thought that the plants might lack the ability to form wound cork as they emerge from dormancy, and that this might account for their increased susceptibility at that time. Cormack (3) demonstrated that wound cork was retarded in roots of alfalfa and sweet clover which had been frozen, and also that it formed very slowly at low soil temperatures, but fairly rapidly during summer, when the temperature is higher.

The present study concerns mainly the relation of wound cork to the invasion of roots by the two pathogens indicated.

Materials and Methods

Inoculation of Plants

In this study four varieties of alfalfa and four of sweet clover were used, each one differing in degree of winter hardiness. The tests were made under both greenhouse and field conditions. In most experiments the roots of vigorous plants grown from seed planted in the field in June were inoculated the following September. In one case vigorous plants were transplanted into boxes, hardened off for a week, then inoculated with *P. meliloti* and artificially frozen at −5° C. for 3 days, after which they were held in a greenhouse at a temperature of approximately 18° C. More satisfactory infection was obtained in the field than under greenhouse conditions. The two pathogenic cultures used were isolated from diseased sweet clover roots. The culture of *Sclerotinia* sp. has not been definitely identified, but Dr. H. H.

[1] *Contribution No. 406 from the Division of Botany, Experimental Farms Branch, Department of Agriculture, Ottawa, Canada, co-operating with the University of Alberta. This paper constitutes one part of a thesis submitted April, 1931, to the University of Alberta in partial fulfilment of the requirements for the degree of Master of Science.*

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Whetzel, who has examined it, has suggested that it may be an undescribed species closely related to *S. minor*. *P. meliloti* has been described by Sanford (9).

In preparing the roots for treatment the soil was removed from one side of each tap root to a depth of 3–4 in., and the surface left clean. The roots of one set of plants were uniformly wounded with a sharp scalpel at the point of inoculation. The roots of an equal number of plants of each variety were treated similarly, except that they were not wounded. For those series inoculated a small amount of oat hull culture of the pathogen was placed on a thin piece of absorbent cotton and packed firmly against each tap root. At regular intervals after treatment, replicate sets of plants of each variety and treatment were removed from the soil for histological examination. The extent of wound cork development beneath lesions and wounds, and the severity of infection were estimated numerically, using values from 0 to 10.

Histological Technique

The inoculated, wounded, or otherwise treated portion of each root to be studied was fixed, infiltrated with paraffin, and sectioned about 10 μ thick. The mounted sections were stained overnight in a 95% alcoholic solution of Sudan III, in a 0.5% aqueous solution of acid fuchsin for about 5 min., and finally in a 0.5% aqueous solution, consisting of 9 parts of light green and 1 part of iodine green, for about 10 min., washing between stains. Good differentiation of cork and other tissue was secured, the cork cells staining orange, the diseased tissues and mycelium pink to red, and the normal tissues blue.

Experimental Results

Observations on Root Structure

Roots of alfalfa and sweet clover have essentially the same structure. The primary cortex of the early seedling stage soon becomes stretched and ruptured by secondary growth, sloughs off, and is replaced by a permanent cork covering which is complete when the plants are about four weeks old. This external cork layer is generally three to five cells wide and forms a practically complete protective covering for the root, except where branch roots pass out and lenticels occur. Such openings are usually protected by deeper lying cork layers, which are at least two cells wide.

Root Penetration by the Pathogens

Sclerotinia sp. Wounded and non-wounded roots were attacked with approximately equal severity, indicating that this pathogen is apparently capable of penetrating through the external cork covering of the roots. Representative results, which are given in Table I, show that this was true with varieties of both alfalfa and sweet clover, although the latter were more severely attacked. Histological examination showed many cases of what appeared to be direct penetration of the uninjured cork wall. The growing hyphae usually accumulated in close contact to the root and gradually broke through the protective cork covering (Plate I, A and B), after which they

surged through into the underlying tissues (Plate I, C). In some instances the underlying cells were disorganized and a dark staining substance was formed below the cork covering before it was completely penetrated by the hyphae (Plate I, A and B). These observations indicate that penetration may have been accomplished partly by hyphal pressure and partly by enzymatic action, as described by Lüdtke (6).

TABLE I

INFECTION CAUSED BY *Sclerotinia* SP. IN WOUNDED AND NON-WOUNDED ROOTS OF *Medicago* AND *Melilotus*, 10 DAYS AFTER INOCULATION

Variety	Infection rating*	
	Wounded roots	Non-wounded roots
Medicago		
Grimm	1.0	1.5
Cossack	1.0	1.5
Baltic	2.0	1.5
Liscombe	1.5	1.0
Melilotus		
White Blossom	9.0	8.5
Arctic	7.0	7.5
Maccor	9.0	7.5
Yellow Blossom	6.0	5.5

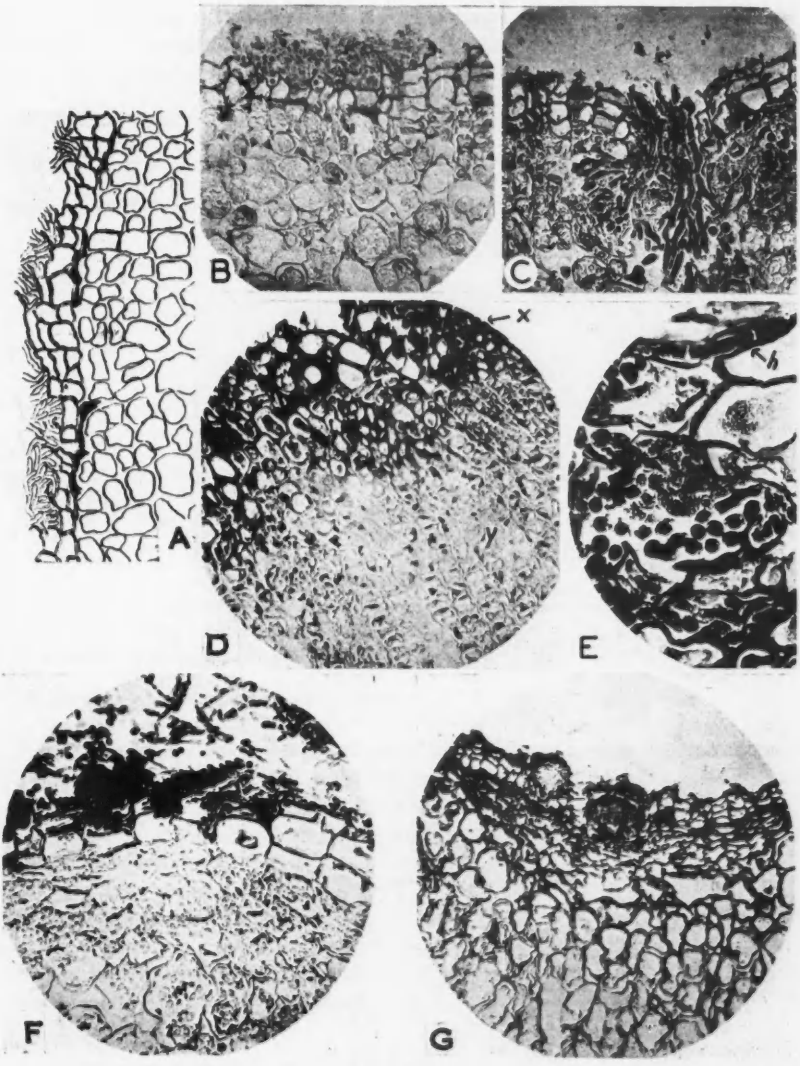
**Average numerical rating of four replicates.*

Plenodomus meliloti. This pathogen also attacked non-wounded roots as readily as those which had been wounded. Histological observations indicated that it penetrated the external cork covering by mass hyphal action, as described by Conant (2). Dense masses of hyphae were often observed in close contact to the disintegrating cork layer (Plate I, F), and frequently pycnidia of the fungus were embedded in the remains of the cork layer after the hyphae had entered the roots (Plate I, G).

Progress of the Pathogens Through the Root Tissues

Sclerotinia sp. After penetrating the roots of either alfalfa or sweet clover, this pathogen often spread rapidly, particularly in the tissues of sweet clover. The hyphae passed both through the cells and between the cells (Plate I, E), and usually made greatest progress parallel to the main axis of the root. Frequently the root tissues were at least partly killed several cells in advance of the pathogen. This was indicated by the staining characteristics and disorganized appearance of the cell contents of the tissue bordering healthy parts (Plate I, D).

An interesting feature was the fact that a complete layer of wound cork seldom occurred in advance of invasion. Such wound cork as formed did not seem to offer appreciable, if any, resistance. In Table II it will be observed that although the roots of sweet clover were attacked much more severely than those of alfalfa, the amount of wound cork formed in the non-inoculated roots was approximately the same. In the inoculated roots, wound cork was severely inhibited or failed to appear when invasion was in progress. Thus, on the basis of the data obtained in this and previous studies (3), it would seem that wound cork does not play a significant role in this root rot, either in the early spring or later in the season. It should be mentioned that in the case of alfalfa it was found, by experiments carried out in midsummer, that sometimes wound cork, several cells in thickness, did



FIGS. A-E. *Sclerotinia sp. A. Hyphae starting to penetrate the uninjured cork covering of an alfalfa root. Note the dark deposits forming below the cork layer. Camera lucida drawing. × about 155. B. Progress of hyphae through the cork covering of an alfalfa root. × 185. C. Hyphae surging into the underlying tissues after penetrating the cork covering. D. Disorganization of the cells (y) in advance of invasion (x) of a sweet clover root. × 108. E. Hyphae within and also between (h) the cells of a sweet clover root. × 270.*

FIGS. F, G. *Plenodomus meliloti. F. Hyphae penetrating the uninjured cork covering of a sweet clover root. × 185. G. Pycnidial formation in the ruptured cork covering of an alfalfa root. × 108.*

form beneath lesions that had made but little progress. Since *Sclerotinia* sp. seldom produced extensive lesions on alfalfa roots (Tables I and II), the presence of this wound cork was not considered very significant in connection with the development of disease under field conditions.

TABLE II

INFECTION AND WOUND CORK DEVELOPMENT IN ROOTS OF *Medicago* AND *Melilotus*, NON-INOCULATED AND INOCULATED WITH *Sclerotinia* SP. AND *P. meliloti*

Variety	Treatment	*Sclerotinia* sp.*		*P. meliloti*†	
		Infection	Wound†† cork	Infection	Wound†† cork
Medicago					
Grimm	Inoculated	1.3	0.3	3.2	0.0
	Non-inoculated	0.0	3.1	0.0	3.2
Cossack	Inoculated	1.2	0.2	3.3	0.0
	Non-inoculated	0.0	2.8	0.0	4.0
Melilotus					
White Blossom	Inoculated	8.8	0.0	2.2	1.5
	Non-inoculated	0.0	3.8	0.0	3.8
Arctic	Inoculated	7.3	0.0	1.9	1.0
	Non-inoculated	0.0	4.1	0.0	3.8

**Field experiment, 10 days after treatment.*

†*Laboratory experiment with plants artificially frozen at −5° C. for 3 days, 13 days after treatment.*

††*Average numerical rating of four replicates.*

Plenodomus meliloti. The hyphae of this pathogen were frequently seen between the cells and also inside of cells of invaded tissues. There was even more marked killing of the tissues in advance of the hyphae than with *Sclerotinia* sp. Also, wound cork was severely suppressed, and in many instances failed to appear even at favorable soil temperatures. In spite of this, the lesions were arrested during early June, when the growing season started. Hence, as in the case with *Sclerotinia* sp., wound cork evidently is not a factor in arresting the progress of the disease. In place of wound cork, a dark brown to black deposit of unknown composition usually appeared between the lesion and the sound tissue of actively growing plants, particularly in older lesions.

Toxic Effect of Pathogens

It has been shown that both *Sclerotinia* sp., and *P. meliloti*, particularly the latter, often kill and disorganize the root tissues in advance of the invading hyphae. The presence of either pathogen also severely retards and often completely inhibits wound cork development in the adjacent tissues. Also, in connection with the penetration of *Sclerotinia* sp. a dark staining substance was sometimes observed below the disintegrating cork covering

of the root. Since these phenomena were observed only in the presence of the pathogens, it is conceivable that they are caused by products of metabolism toxic to the root tissues.

The nature of the toxic substances concerned is unknown, but it was thought that the pH relationships might be important. Herklots (4) found that acidity up to pH 4.6 promoted the formation of cork in the potato tuber, but delayed its subsequent suberization, while a reaction of pH 7.5 and higher promoted suberization, but retarded meristematic activity. The reaction of alfalfa and sweet clover roots invaded by *Sclerotinia* sp. and by *P. meliloti*, and of the healthy root tissues of similar plants, was determined electrometrically with a quinhydrone electrode, using a small amount of distilled water to make a solution of the tissue. The average reaction of healthy roots of alfalfa and sweet clover was pH 6.2 and pH 6.4, respectively. Roots of alfalfa invaded by *Sclerotinia* sp. gave a reaction of pH 5.4, while those of sweet clover had a pH value of 4.9. There was no significant change in the reaction of roots invaded by *P. meliloti*. Zeliff (13) states that the optimum reaction for growth of *S. sclerotiorum* is pH 3.2, and Sanford (9) states that the optimum for *P. meliloti* is pH 6.2. Thus, it would appear that the reaction of the invaded tissues depends to some degree on the optimum for growth of the pathogen concerned.

Discussion

Several important points in the foregoing data may be emphasized, and their relation to the problem evaluated. In the first place, both pathogens appeared to penetrate the root covering which consists of several layers of well suberized cork cells. Secondly, wound cork was, as a rule, practically suppressed in the presence of either pathogen, and there was often killing of the tissues in advance of the invading hyphae of both. Finally, there is the question as to why the advance of *P. meliloti* is checked when the plants regain their summer vigor during June or later, while progress of *Sclerotinia* sp., although retarded, is not completely checked.

It is common knowledge that pathogenic fungi penetrate with difficulty and are frequently arrested by adequately suberized cork layers. Priestley (8) found that the suberin impregnating cork walls was unmixed with cellulose, and could not be decomposed by the ordinary hydrolyzing enzymes excreted by parasitic fungi. Jones (5) observed that *Actinomyces scabies* was able to pass through the suberized barriers in the potato tuber by growing in the unsuberized middle lamella of the cell walls. Matsumoto (7) reviewed most of the important early work on cell penetration by pathogenic fungi. His studies showed that *Rhizoctonia solani* penetrated directly through the cuticle of plants and that this was chiefly a mechanical process. Brown and Harvey (1) concluded that pathogenic fungi could penetrate the plant cuticle only in a purely mechanical way. On the other hand Lüdtke (6) found that the penetration of pathogens into host plants was effected partly by mechanical means and partly by enzymatic action, which conclusion is supported by the

recent studies of Thomas (11) on the parasitism of *Armillaria mellea*. Conant (2) concluded that the enzymes produced by the aggregated hyphae of *Thielavia basicola* could break down the suberized tissues of tobacco roots, allowing the fungus to break through the weakened cork walls. Our infection studies and histological observations have given unmistakable evidence that *Sclerotinia* sp., and *P. meliloti* can penetrate the cork covering of alfalfa and sweet clover roots in the absence of either lenticels or wounds. While there are indications that the hyphae of these pathogens excrete enzymes and also evidence of mass hyphal pressure in penetrating the cork layers, a decision as to which is more effective cannot be made on the data given.

With regard to the observed suppression of wound cork and other abnormal effects, a number of fungi are known to have a toxic effect on plant tissues in advance of hyphal invasion. Tubeuf and Smith (12), in discussing *S. sclerotiorum*, quote from an early paper by De Bary as follows: "The dead parts of the plants serve as nutriment to the fungus, which makes its way into the tissues and causes death of cells in direct contact or immediate neighborhood. The deadly fluid separated by the fungus contains, as an essential constituent, an enzyme soluble in acid solutions and capable of dissolving the cell walls; also a number of imperfectly known organic and inorganic acids and salts, amongst which oxalates can certainly be proved". As mentioned previously, the hyphae of both *Sclerotinia* sp. and *P. meliloti* had a definite effect on the tissue in advance of invasion. If this is due to metabolic products which are quickly or even slowly lethal to normal cell function, it is conceivable that meristematic activity necessary to the initiation of wound cork might be greatly retarded or definitely suppressed. The reaction of the invaded tissues would seem to be of doubtful importance in relation to the toxic effects of the pathogens, since the change in reaction observed did not differ greatly from normal.

There is no doubt that alfalfa and sweet clover are most susceptible to both *Sclerotinia* sp. and *P. meliloti* following the winter dormancy period, and also that these plants are not attacked by the latter pathogen after the growing season has started. While mechanical injury may increase infection in certain instances, this study has demonstrated that penetration is by no means dependent on this type of injury. At the low soil temperatures which prevail during April and May, wound cork forms very slowly, and even if there were no other complicating factors, such as the suppression of it in the presence of the pathogen, it is doubtful if the progress of these pathogens would be materially affected. Possibly later in the season at higher soil temperatures wound cork might play a role in checking *Sclerotinia* sp. during the early stages of invasion, but, as Thomas (11) suggests in the case of *Armillaria mellea*, such wound cork might not be effective. However, should such lesions become extensive, wound cork would be immediately arrested, and become an unimportant consideration. Consequently, the general conclusion is that in Alberta during April, May, and possibly June, wound cork plays a negligible role, while during summer months it may aid

in arresting incipient lesions caused by *Sclerotinia* sp. or by certain weak parasites, which may not excrete substances unfavorable to wound cork development.

No explanation can be offered as to why lesions caused by *P. meliloti* during early spring cease to make further progress during summer. At least wound cork is absent or negligible in quantity. Whether at higher temperatures the dark brown to black deposit bordering the lesions becomes a barrier, or whether certain physiological conditions which occur only in the more actively growing plants are responsible, is not clear at this time.

Acknowledgments

The writer is greatly indebted to Dr. G. B. Sanford, Pathologist-in-Charge, Dominion Laboratory of Plant Pathology, at the University of Alberta, Edmonton, for suggesting the problem and for helpful advice and criticisms throughout this study; also to Dr. A. W. Henry, Associate Professor of Plant Pathology, University of Alberta, for valuable suggestions.

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ISOLATION OF S AND R TYPES BY CATAPHORESIS[1]

By G. B. Reed[2] and B. G. Gardiner[3]

Abstract

It is shown that by taking advantage of the differences in cataphoretic velocities it is possible to separate S and R types of certain acid-fast species of bacteria.

It has been previously demonstrated (Reed and Gardiner (7)) that there is a definite difference in electrophoretic charge between the S and R forms of *Mycob. leprae* described by Reed (6). This difference was correlated with differences in their isoelectric points and their tendency to be agglutinated in acid suspensions. Similar differences in the cataphoretic speed of S and R types of the tubercle bacillus have been shown by Kahn and Schwarzkopf (3). This is in line with the extensive investigations of Falk (2), Chapman (1), Rosenow (8) and others on different species of bacteria.

The work of Kligler and his colleagues (4, 5) shows that various viruses suspended in buffered solutions can be recovered at the anode after cataphoresis, apparently being carried there by the associated proteins. This suggested that a similar method might serve to separate S and R forms, at least in cases where there exists a demonstrable difference in the cataphoretic rate.

An apparatus was set up, as shown in Fig. 1, consisting essentially of two chambers, *A*3 and *C*3, which were filled to the same level with physiological saline and connected by a rather large siphon. Each of them was connected by a potassium chloride agar bridge to another chamber, and eventually to a non-polarizable electrode. In this case copper electrodes in copper sulphate solution were used. These were connected with the 120-volt, direct-current line. An impressed voltage of 220 resulted in enough heating to kill the bacteria eventually while a voltage less than 120 resulted in a migration too slow to give satisfactory results.

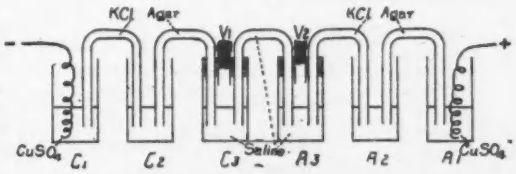

FIG. 1. *A cataphoretic chamber for the isolation of R and S forms of bacteria, A1 and C1, Cu–$CuSO_4$ electrodes connected with KCl agar bridges to KCl chambers A2 and C2 which in turn are connected by agar bridges to cathode chamber C3 and anode chamber A3 communicating by a siphon. Vents for introducing organisms are shown at V1 and V2.*

The chambers *A*3 and *C*3 were autoclaved, together with the physiological saline and the connecting siphon. Openings for the agar bridges were plugged during this operation. Sterile potassium chloride agar bridges were then inserted and the assembled apparatus tested for sterility.

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Pure S and R types of *Mycob. leprae*, 513, were grown on Petragnani's medium. After seven days' growth suspensions of equal density of the two types were made in physiological saline. Equal amounts of these suspensions were then mixed in a sterile tube and centrifuged. The supernatant was then removed, and the organisms resuspended in a few drops of physiological saline. One drop of this mixed and concentrated suspension was added with a sterile Pasteur pipette to the chamber *C*3 through the vent *V*1; at the same moment, in order to eliminate any slight siphoning action, one drop of sterile saline was added to the chamber *A*3 through the vent *V*2. At intervals both before and after the current was turned on, samples were removed through the vents by means of a sterile platinum loop and streaked directly on Petragnani's medium. Colony counts of these cultures were made after seven days' growth.

Table I shows a typical set of results. The S organisms appeared at the anode chamber first, in something less than 30 min., while the R organisms did not arrive there until after about 45 min. Before the current was turned on, a culture from the cathode chamber showed approximately equal numbers

TABLE I

EFFECT OF CATAPHORESIS IN SEPARATING S AND R TYPES OF *Mycob. leprae, 513*

Time exposed to current	Type of colonies from cathode	Type of colonies from anode
0	R and S, approx. equal	Sterile
15 min.	R and S, approx. equal	Sterile
30 min.	R and S, approx. equal	S only, several hundred colonies
45 min.	R and S, approx. equal	Several hundred S, one R colony
1 hr.	Mixed S and R	Mixed S and R
2 hr.	Mixed S and R	Mixed S and R
4 hr.	Mixed S and R, but somewhat more R	Mixed S and R
12 hr.	118 R colonies, 20 S colonies	Mixed S and R

TABLE II

EFFECT OF CATAPHORESIS IN SEPARATING S AND R TYPES OF PETROFF'S STRAIN OF *Mycob. tuberculosis avium*

Time exposed to current	Type of colonies from cathode	Type of colonies from anode
0	R and S, approx. equal	Sterile
15 min.	R and S, approx. equal	Sterile
30 min.	R and S, approx. equal	18 S colonies
1 hr.	R and S, approx. equal	Several hundred S, 3 R colonies
2½ hr.	Mixed S and R	Mixed S and R
5 hr.	Mixed S and R	Mixed S and R
10 hr.	Mixed S and R	Mixed S and R
20 hr.	Mixed S and R	Mixed S and R

of S and R colonies, while after 12 hours' treatment the R colonies outnumbered the S by six to one. This result amply confirms the previous findings as to the cataphoretic speed of the two types.

By the same technique, similar experiments were performed using R and S strains of Petroff's avian tubercle bacillus. A typical set of results is given in Table II. The general trend was similar to the results with *Mycob. leprae* but the movement toward the anode was slightly slower. This is in agreement with the finding that the cataphoretic movement of the avian tubercle bacilli is slower than the *Mycob. leprae.*

Although the results render it highly improbable that siphoning or similar current action had any appreciable effect, a control was run to eliminate this possibility. This was done by placing the organisms in the anode chamber *A*3 instead of cathode chamber, *C*3. On examination, cultures from *A*3 made at varying intervals up to 24 hours all showed mixed S and R colonies, while those from *C*3 were consistently sterile.

Conclusions

An apparatus has been described, resembling one used by Kligler in virus work, in which a mixture of S and R forms of *Mycob. leprae* and avian tubercle bacilli were separated by taking advantage of the differences in cataphoretic velocity of the two types.

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ON THE ACOUSTIC RADIATION FIELD OF THE PIEZO-ELECTRIC OSCILLATOR AND THE EFFECT OF VISCOSITY ON TRANSMISSION

PART II[1]

By L. V. King[2]

Abstract

Numerical data on the distance of transmission of sound in sea water from a 10-in. piezo-electric oscillator are discussed in the light of theoretical results obtained in a previous paper. It is shown how by the principle of similitude the chart for transmission at optimum wave-length calculated for a 50-watt, 60 cm. oscillator can be used for a transmitter of any given diameter and output. A comparison with some experiments of Boyle's points to the fact that at supersonic frequencies, in the neighborhood of 100,000 cycles, a considerably higher coefficient of viscosity than that obtained by flow methods must be used.

Very few data on the performance of actual piezo-electric oscillators have been published. The writer is indebted to Dr. R. W. Boyle for numerical data and valuable criticism enabling some comparison to be made between observation and the numerical data employed to illustrate formulas derived in this paper.

The coefficient of viscosity of sea water was measured by the capillary flow method and was found to be 0.017 at 7.3° C. Interpolation between the values $\mu_0 = 0.0181$ at 0° C. and $\mu_{20} = 0.0101$ at 20° C., calculated from tabulated values for sodium chloride solution of density 1.024, gives $\mu_{7.3} = 0.016$, in good agreement with Dr. Boyle's determination.

In former unpublished tests carried out in sea water it was found that a 10-in. disk at a frequency of 100,000 gave at 2½ miles a moderately strong signal estimated from reception by a piezo-electric receiver to correspond to a displacement amplitude of 3×10^{-10} cm. in the water. This enables us to estimate the velocity amplitude and output of the transmitter. If we denote by $|\xi|$ the displacement amplitude in the central beam, we easily deduce from the formulas of Section 11 (3) that

$$|\dot{\xi}| = \frac{1}{2} \frac{a^2}{c} |\ddot{\xi}| \frac{e^{-\kappa' r}}{r} . \tag{1}$$

Using the above data supplied by Dr. Boyle for the 10-in. oscillator transmitting at 100,000 cycles, we have, $a = 12.8$ cm., $\kappa_0 a = 53.9$, $|\xi| = 3 \times 10^{-10}$ cm., $r = 2\frac{1}{2}$ miles $= 4 \times 10^5$ cm., $\mu_7 = 0.017$, $c = 1.49 \times 10^5$, $\kappa_0 = \omega/c = 4.20$.

From Equation 68 (3) we have

$$\kappa' = \frac{2}{3} \frac{\mu \kappa_0^2}{c \rho_0} = 1.30 \times 10^{-4} .$$

[1] *Manuscript received July 26, 1934.*
Contribution from the Department of Physics, McGill University, Montreal, Quebec, Canada.
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Solving for $|\dot{x}|$ in Equation (1) we find that $|\dot{x}| = 0.366$ cm./sec. According to Equation 72 (3) the output is $[dW/dt] = \frac{1}{2}\pi a^2 \rho_0 c |\dot{x}|^2 = 0.524$ watt, giving a transmission per unit area of 0.00102 watt/cm^2. According to Equation 79 (3) the axial intensity is given by

$$I(0) = \frac{e^{-2\kappa' r}}{r^2} \frac{(\kappa_0 a)^2}{4\pi} \left[\frac{dW}{dt}\right] = 0.273 \times 10^{-9} \text{ erg/cm.}^2$$

On the decibel scale this corresponds to a reception level of 64.3 db.

These results, deduced from observation, may be compared with the numerical data employed in the writer's paper as shown in Table I.

TABLE I

CHARACTERISTICS OF PIEZO-ELECTRIC TRANSMITTERS

—	60-cm. oscillator (theory)	10-in. oscillator (estimated from observations)
Total output	50 watts	0.524 watt
Circumference/wave-length	50	53.9
Transmission per unit area	0.0177 watt/cm.^{2}	0.00102 watt/cm.^{2}
Velocity amplitude of piston	1.53 cm./sec.	0.366 cm./sec.

Originally, in the absence of numerical data, the amplitude of the 50-watt oscillator was chosen to make the maximum pressure-amplitude at the centre of the disk less than atmospheric (or cavitation) pressure by a factor of safety of 4, according to Formula 40*(3).

In order to have a useful optimum chart, reception intensities require to be condensed by the use of a logarithmic scale. This is conveniently provided for by the decibel scale now in international use. It is also necessary to refer the chart to some standard diameter and output of the transmitter, such as 60 cm. and 50 watts, although these specifications and ranges implied are probably considerably greater than those prevailing in present practice. As it stands it provides an objective for designers of practical transmitters. It may, however, by the principle of similitude, be used for a transmitter of any given radius and output. For a given intensity of reception, let r' be the optimum range of a transmitter of radius a' and output $[dW'/dt]$ at optimum wave-length λ'. It follows from Equations 81 and 80 (3) that

$$\left(\frac{r'}{r}\right)^3 = \left(\frac{a'}{a}\right)^3 \frac{[dW'/dt]}{[dW/dt]} \quad \text{and} \quad \frac{\lambda'}{\lambda} = \left(\frac{r'}{r}\right)^4. \tag{2}$$

To use these formulas in relation to the optimum reception chart of Fig. 2, we take $a = 30$ cm. and $[dW/dt] = 50$ watts, and determine r and λ corresponding to the desired reception level, interpolating between the 0° and 20° C. curves for the given sea temperature. The procedure will be made clear by finding the theoretical optimum range and wave-length for 64.3 db. reception

* *The wide divergence in the above figures for transmission per unit area shows the need for observations on the maximum output of an actual piezo-electric transmitter consistent with absence of cavitation (1).*

from the 10-in. transmitter of 0.524 watt output referred to in Table I. From the chart we find by interpolation that at 7° C., we have for $a=30$ cm., $[dW/dt]=50$ watts, $r=34$ km., $\lambda=4.0$ cm. Then, according to Formulas (2) above,

$$\left(\frac{r'}{34}\right)^3=\left(\frac{12.8}{30}\right)^3\frac{0.524}{50},\ \text{giving}\ r'=4.09\ \text{km.}\ \text{and}\ \frac{\lambda'}{4.0}=\left(\frac{4.09}{34}\right)^{\frac{1}{2}},\ \text{or}\ \lambda'=1.39\ \text{cm.}$$

corresponding to a frequency $f=107{,}000$.

These results show from the observational data supplied by Dr. Boyle that the transmitter was operating close to theoretical optimum conditions.

The use of the decibel scale in estimating reception is practically convenient because many data are now available as to intensity levels susceptible of measurement and transmission in air. For instance a level of 64 db. is somewhat less than that of an average voice speaking into a telephone transmitter, and is thus known to possess sufficient energy to be susceptible of easy measurement.

The level of 30 db., assumed in the curves of Fig. 1, as a probable lower limit of detectable intensity was estimated by the writer from experience with sound-measuring instruments in air. It was found that a Webster phonometer used in measuring the strength of fog signals would give an easily audible, detectable reading of 0.1 mm. for a pressure variation $|\delta p|=0.000204$ bar (2, p. 249). This corresponds to a level of 50 db. The disk of the instrument was purposely loaded to make it insensitive; it was estimated that by suitable adjustment its sensitivity could have been increased by a factor of 10, corresponding to a level of 30 db. It therefore appears probable to the writer that a piezo-electric receiver, designed to make best use of mechanical resonance, and utilizing high amplification, should be capable of detecting a reception level of 30 db. in water; in all events this should be the objective for the design of such a receiver. When the reception level of the receiver is known and the output and radius of the transmitter are given, a set of curves corresponding to those of Fig. 1 are easily computed from Formula 79 (3).

The important feature of an optimum transmitting frequency for a given range of transmission was first pointed out by Dr. Boyle in 1918, although arrived at independently by the writer as a theoretical consequence of the effect of viscosity on transmission. Quoting from a report of tests carried out in 1918 he states:

"The theoretical results brought out here, namely, that for any given distance there is a best frequency at which to transmit, and also that for long distances the lower frequencies will travel better than the higher ones (*i.e.*, will be less damped out by the viscosity) receive a good deal of experimental support from our experiments.

For work in the open sea over the greater part of the year, the temperature of the water will be higher than the temperature considered here, *viz.*, 7° C. The coefficient of viscosity therefore will be less than the value used here (0.017), and therefore the best frequencies will have values slightly higher

than those represented here; also, waves of any frequency ought to travel better in the summer than in the winter. Another fact to be taken into consideration is that in any practical supersonic system a part of the energy reaching the receiver is due to the supersonic waves reflected from the water surface. The path of such waves between transmitter and receiver must necessarily be larger than that of the direct waves, and on this account the frequency could with advantage be lowered a little.

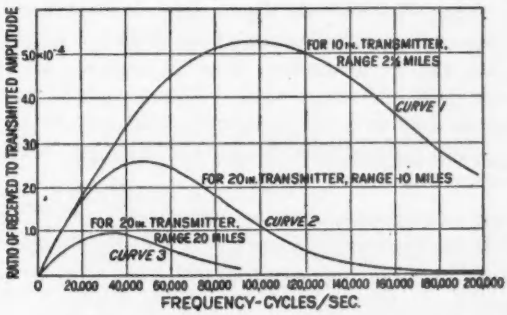


FIG. 1. *Calculated ratio of received to transmitted amplitude. (Courtesy of Dr. Boyle).*

In conclusion it must be stated that these calculations can be approximate only, since it is impossible to say how far the first assumption of paragraph 1* is justified for waves of such high frequencies as are used in supersonics. But the results seem to agree with the practical observations that waves of lower frequency travel better than those of very high frequency, and consequently in endeavoring to obtain ranges of five miles or upwards it will be necessary to work at frequencies of about 70,000 cycles per sec. and lower, unless large amounts of energy can be put into the water."

Figs. 1 and 2 show curves which Dr. Boyle has very kindly allowed the writer to include in this paper.

To compare these results with the writer's formulas, we note from Equation (1) that, writing $|\dot{x}| = \omega|x|$ we have

$$\frac{|\xi|}{|x|} = \frac{1}{2} a^2 \kappa_0 \frac{e^{-\kappa' r}}{r} \quad . \tag{3}$$

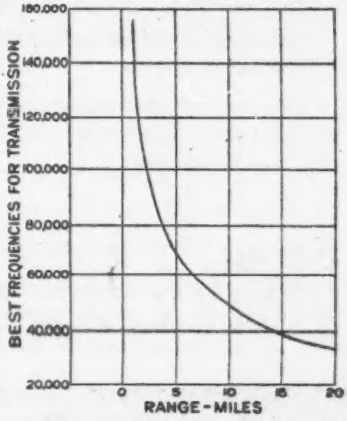


FIG. 2. *Optimum frequencies for transmission (calculated).*

It is readily proved that assuming $|x|$ constant as the frequency is varied, the ratio $|\xi|/|x|$ for a given r has a maximum for $\lambda = 4\pi\left(\frac{\mu r}{3\rho_0 c}\right)^{\frac{1}{2}}$ as in Equation 80 (3). With $r = 4 \times 10^5$ cm., $\mu_7 = 0.016$, $\rho_0 c = 1.53 \times 10^5$, we find $\lambda = 1.48$ cm., corresponding to a frequency $f = 100{,}000$. With this value of λ we find

$$\frac{|\xi|}{|x|} = \frac{\pi a^2}{\lambda r \sqrt{e}} = 5.26 \times 10^{-4} \quad .$$

* *i.e., the use of the coefficient of viscosity obtained from steady flow measurements.*

It will be noticed that these values of f and $|\xi|/|x|$ agree as closely as could be desired with the maximum of the curves calculated by Dr. Boyle (Figs. 2 and 3) for the 10-in. transmitter with a range of $2\frac{1}{2}$ miles.

Dr. Boyle points out that in practice the best signals from a 10-in. transmitter at $2\frac{1}{2}$ miles come in over a range of frequencies from 50,000 to 80,000. A value of μ_7 double that assumed from capillary flow experiments would make the optimum frequency come out about right. This to some extent supports Biquard's contention alluded to in Section 12 (3), that the effective viscosity at supersonic frequencies is considerably greater than the values usually assumed.

On the other hand, Equation (3) presupposes the existence of an infinite rigid flange; it is possible that the appropriate formula for a flangeless transmitter would give an optimum frequency in better accord with observation with the usual value of viscosity.

The determination of the optimum wave-length from Equation (3) also assumes that the transmitter amplitude $|x|$ remains constant as the frequency is varied. Should $|x|$ be a function of the frequency, as might well be the case if the transmitter is operated near its natural resonance in spite of a constant applied voltage, the frequency corresponding to maximum displacement-amplitude $|\xi|$, or signal strength would be shifted to the right or left of that calculated for constant transmitter amplitude $|x|$ and the usual value of the coefficient of viscosity.

It is evident that accurate data on the coefficient of viscosity of sea water at supersonic frequencies are greatly needed in connection with the practical application of theory.

References

1. Boyle, R. W., Taylor, G. B. and Froman, D. K. Trans. Roy. Soc. Can. 23, III : 187-201. 1929.
2. King, L. V. Phil. Trans. Roy. Soc. Lond. 218 A : 211-293. 1919.
3. King, L. V. Can. J. Research, 11 : 135-155. 1934.

EXPERIMENTS ON THE USE OF MIXTURES OF GASOLINE WITH ETHYL AND ISOPROPYL ALCOHOLS IN INTERNAL COMBUSTION ENGINES[1]

By M. S. Kuhring

Abstract

The paper covers engine tests conducted on gasoline and various mixtures of isopropyl and ethyl alcohols with gasoline. Comparisons were made with additions of lead tetraethyl in the gasoline. The tests were conducted in two separate groups and included octane number, power, consumption, and highest useful compression ratio.

It is shown that once detonation is suppressed in an engine, little or no further increase in power may be expected by raising the anti-knock value of the fuel, without also raising the compression ratio.

In the first group, specific fuel consumptions when using the ethyl alcohol–gasoline mixtures were higher than when gasoline only was used. This holds for fuels *A* and *C*. In the case of fuel *B* the specific consumption was found to be almost the same whether or not the alcohol was used.

When lead tetraethyl was added to an alcohol–gasoline mixture, there was a further increase in anti-knock value, but this increase was not as great as when the lead was added to the same gasoline without alcohol.

In group 2, specific fuel consumptions for gasoline–alcohol mixtures were higher than for gasoline only. In the 10% alcohol mixtures, consumptions were higher when ethyl alcohol was used than when isopropyl alcohol was mixed with the gasoline. In the 20% alcohol mixtures, the ethyl alcohol consumptions were still somewhat higher than those of the isopropyl mixtures; but with the 30% alcohol mixtures, specific consumptions were higher for the isopropyl alcohol additions than for ethyl alcohol additions.

Octane numbers, which were determined under C. F. R. Motor Method procedure, showed the ethyl alcohol to be superior as a knock inhibitor, but when the Highest Useful Compression Ratio was determined (under low cylinder temperature conditions) the 10% and 20% concentrations of isopropyl alcohol were found to be superior to ethyl alcohol in the same proportions. Above this concentration, ethyl alcohol became more effective than equivalent additions of isopropyl alcohol.

Range of Investigation

A report on the economic and technical feasibility of using as a motor fuel in Canada, gasoline mixed with alcohol made from grain, has been issued by the Division of Chemistry of the National Research Council (2). The experiments recorded in the present communication, which have been referred to briefly in the above report, deal with the effect on the operation of internal combustion engines of adding various proportions of ethyl and of isopropyl alcohol to representative samples of gasoline, and include a comparison of the relative effectiveness of additions of alcohol and lead tetraethyl on knocking. The effect of alcohol admixtures on the water tolerance of gasoline is the subject of a separate communication by Bayley and Hopkins (1). The work was conducted under two different sets of conditions, and the gasolines with which alcohol mixtures were made were not similar, consequently the two groups of tests will be treated separately.

[1] *Original manuscript received July 3, 1934.*

Contribution from the Engine Laboratory, Division of Physics and Engineering, National Research Laboratories, Ottawa, Canada.

Group 1

Three samples of gasoline obtained for this work were as follows:

A. Straight run aviation gasoline, non-ethyl.

B. Cracked, casing-head blend, non-ethyl.

C. Similar to sample *B*.

No definite information was obtained as to the source or properties of these fuels, but they were commercial grades as sold on the open market. Test samples were made up by mixing these fuels with 99.75% ethyl alcohol (See Table I).

Methods and Apparatus

The anti-knock quality, or octane number, of the various fuels was determined on the Ethyl Gasoline Corporation Series 30B detonation engine. This equipment consists of a single-cylinder, liquid-cooled engine, coupled to a synchronous motor with a vee belt. Speed may be varied by changing the pulley on the synchronous motor. Cooling liquid temperature is governed by a fractionating column and condenser, and may be set at any point between 212° and 390° F. Change in compression ratio is accomplished by inserting shims between the cylinder base and the crank case. The compression pressure used for testing the various samples was changed when necessary to give the same knock intensity at full throttle. Knock intensity was indicated by the Bouncing Pin and Knock Meter.

The anti-knock quality of the samples was determined under two sets of conditions, that is, cooling liquid temperature 212° F. and engine speed 600 r.p.m.; and C.F.R. Motor Method (cooling liquid 345° F. and engine speed 900 r.p.m.). In both cases the intake air was at room temperature.

Power curves, throttle curves, consumption, and highest useful compression ratio (H.U.C.R.) were determined on the Armstrong Whitworth variable compression fuel research plant.

This apparatus consists of a single-cylinder, variable-compression, water-cooled engine coupled to an electrical swinging-field dynamometer. Fuel consumption was measured by means of a flow meter.

Gum tests were conducted by the copper dish method.

Octane Number

The octane numbers of the three gasolines and of their mixtures with alcohol were determined by the C.F.R. Research and C.F.R. Motor Methods on the Series 30B engine.*

The results of these tests are shown in Table I and Fig. 1. The solid lines show the octane numbers obtained by the C.F.R. Motor Method, the dotted lines those determined by the C.F.R. Research Method. The difference in octane number under the two sets of conditions becomes less as the proportion of alcohol is increased.

**C.F.R. (Co-operative Fuel Research) Research Method calls for a cooling liquid temperature of 212° F. and an engine speed of 600 r.p.m. For the Motor Method, when using the Series 30B engine, it is necessary to have a cooling liquid temperature of 345° F. and an engine speed of 900 r.p.m. with the air intake at room temperature.*

TABLE I

INCREASE IN OCTANE NUMBER AND H.U.C.R. WITH ALCOHOL ADDITION

Sample No.	Fuel and percentage by vol.		Ethyl alcohol % by vol.	Octane number		H.U.C.R.
				C.F.R. Research Method*	C.F.R. Motor Method**	
1	*A*,	100	0	68	63	6.10 : 1
2	*A*,	95	5	71	67.5	6.25 : 1
3	*A*,	90	10	75	72	6.40 : 1
4	*A*,	85	15	79	76.5	6.82 : 1
5	*B*,	100	0	67	61.5	5.90 : 1
6	*B*,	95	5	70	66	6.00 : 1
7	*B*,	90	10	74	70.5	6.10 : 1
8	*B*,	85	15	78.5	75	6.40 : 1
9	*C*,	100	0	65	61	5.83 : 1
10	*C*,	95	5	67.5	66.4	5.90 : 1
11	*C*,	90	10	71.5	70.4	6.00 : 1
12	*C*,	85	15	76.5	75	6.26 : 1

**Co-operative Fuel Research, Research Method for Series 30B engine, 212° F., 600 r.p.m.*
***Co-operative Fuel Research Motor Method for Series 30B engine, 345° F., 900 r.p.m.*

It may appear unusual for straight run gasoline to show a greater loss in octane number than the cracked gasoline *C*, but as noted above, no tests were conducted to show what proportion of unsaturated hydrocarbons or benzol was present in any of these fuels.

It might also be mentioned in passing, that while it is not customary to

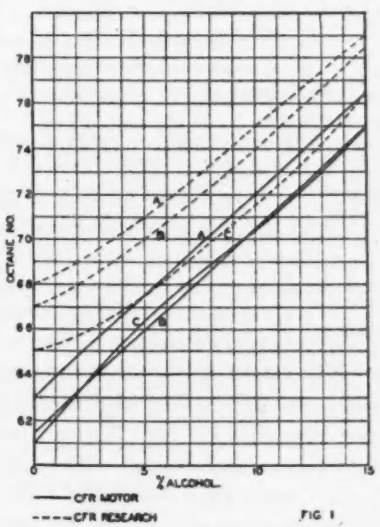


FIG. 1. *Increase in octane number with alcohol addition.*

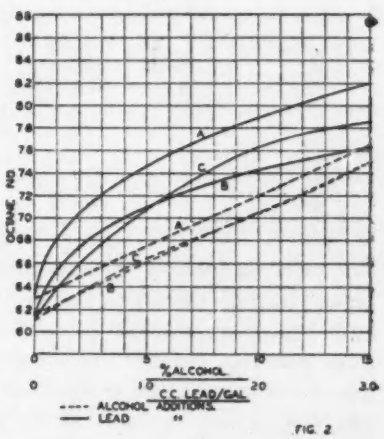


FIG. 2. *Increase in octane number with alcohol or lead tetraethyl addition.*

report knock ratings to less than one octane number, in these tests the readings have been reported to less than one octane number if the test so indicated.

There appears to be a slight irregularity in the Motor Method curve for Fuel *C* where it crosses and recrosses the Fuel *B* curve, but this point was carefully rechecked with no change in result. It would appear that in each of the three fuels the addition of alcohol produced much the same gain in anti-knock quality.

TABLE II

INCREASE IN OCTANE NUMBER WITH ADDITION OF LEAD TETRAETHYL

Lead addition cc. per gal.	Octane number		
	Fuel *A*	Fuel *B*	Fuel *C*
0.0	63	61.5	61
1.0	74.6	71	70.8
2.0	79	74.3	76.3
3.0	82	76.3	78.5

Comparison of the Effects of Alcohol and of Lead Tetraethyl Additions on Knock Rating

The fuels *A* (Sample 1), *B* (Sample 5), and *C* (Sample 9) were treated with lead tetraethyl in the proportions of 1.0, 2.0, and 3.0 cc. per gallon and the octane number determined (Table II).

These results, obtained under the C.F.R. Motor Method, are shown in Fig. 2, in which the vertical ordinates show *either* the percentage of alcohol addition *or* the number of cubic centimetres of lead tetraethyl per gallon.

The effect of lead tetraethyl addition in conjunction with alcohol has been examined in one case where 3.0 cc. of lead tetraethyl was added to the 85–15% mixture of Fuel *A* (Sample 4). (Table III.)

TABLE III

INCREASE IN OCTANE NUMBER OF FUEL *A* DUE TO ADDITION OF ALCOHOL AND/OR LEAD TETRAETHYL

Gasoline *A*, %	Alcohol, %	Lead tetraethyl, cc. per gal.	Octane number
100	—	—	63
85	15	—	76.5
100	—	3	82.0
85	15	3	87.3

This effect is also illustrated by the point in the upper right-hand corner of Fig. 2.

Highest Useful Compression Ratio (H.U.C.R.)

The H.U.C.R. for each of the 12 samples was determined on the Armstrong Whitworth engine. The engine was run at a compression ratio low enough to avoid detonation. The air-fuel ratio was set at the leanest mixture for maximum power. The compression ratio of the engine was then increased, the speed being kept constant, until the power reached a maximum and began to fall off. The air–fuel ratio was then checked and the compression ratio again tested. This compression ratio was taken as the Highest Useful Compression Ratio (H.U.C.R.). The engine was operated at a cooling temperature of 210° F. for both cylinder jacket and cylinder head, and at a speed of 750 r.p.m. (For results see Table I and Fig. 3.)

Power and Throttle Curves

Power, throttle and consumption curves were taken on the Armstrong Whitworth variable compression engine. For the power curves, the engine was operated at full throttle power at 750 r.p.m. and the fuel consumption and developed power noted. The engine was then braked down in 100 r.p.m. steps by means of the dynamometer. After constant temperature conditions had been attained, power and consumption readings were taken at each 100 r.p.m. interval. The throttle remained locked in its full open position during this test.

For throttle curves, the engine was operated at full throttle power, and set at 750 r.p.m. by means of the dynamometer. The dynamometer control was then locked and the engine speed governed by closing the throttle. Consumption figures were not taken for throttle curves.

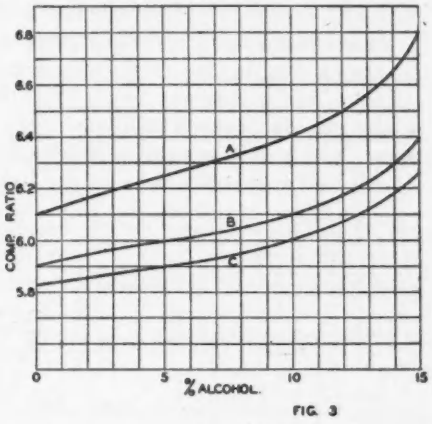
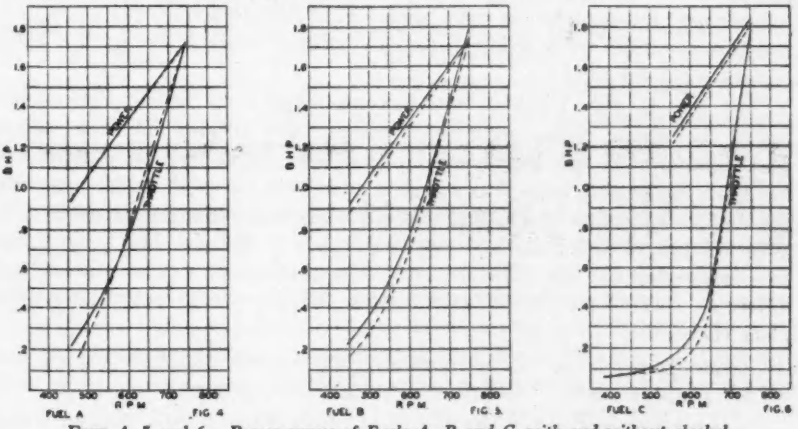


FIG. 3. *Increase in H.U.C.R. with alcohol addition.*

Tests were conducted on:

Sample 1 (Fuel *A*).
Sample 4 (Fuel *A* 85%, alcohol 15%).
Sample 5 (Fuel *B*).
Sample 8 (Fuel *B* 85%, alcohol 15%).
Sample 9 (Fuel *C*).
Sample 12 (Fuel *C* 85%, alcohol 15%).

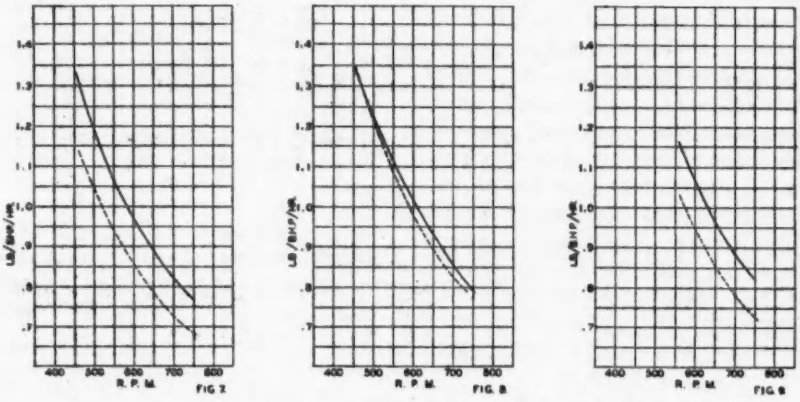
Figs. 4, 5 and 6 show power and throttle curves for the fuels and mixtures



FIGS. 4, 5 and 6. *Power curves of Fuels A, B and C, with and without alcohol.*

respectively, while Figs 7, 8 and 9 show specific consumptions for the power curves. Solid lines indicate alcohol–gasoline mixtures while broken lines indicate gasoline only. Power has been corrected to 60° F. as the air intake temperature was subject to quite wide variation. Fuel consumptions are given for power curves only and are expressed in lb./B.H.P./hr.

As it is not feasible to change the compression ratio of automobiles already in use, it was decided to use one compression ratio for power curves of all samples, and in this way to see what the effect of the various fuels would be under certain engine conditions. For this reason, the power obtained in some cases is not as high as it would have been had advantage been taken of the high anti-knock value of the fuel, to increase the compression ratio.



FIGS. 7, 8 and 9. *Specific fuel consumption curves for Fuels A, B and C and mixtures.*

A compression ratio of 6 : 1 was selected. This is not as high as that employed in some engines but is higher than the average. In addition, this compression ratio marks the point where Fuel *A* without alcohol (Sample 1) resists detonation, while Fuels *B* and *C*, without alcohol (Samples 5 and 9 respectively) detonate.

Fuel A. As stated before, this fuel was capable of resisting detonation under the above engine conditions, without any alcohol addition. From past experience in this laboratory,* it has been found that once detonation has been suppressed, little if any gain in power can be expected by increasing the anti-knock value of the fuel without also raising the compression ratio. This is strongly supported by the power curve in Fig. 4. The same is true to a large extent in the throttle curve, though there is a certain amount of difference due to the difficulty in setting the throttle in exactly the same place each time.

Consumption of the alcohol–gasoline mixture was definitely higher than of the gasoline alone. When considering these consumptions, it must be

**Unpublished Report P.A.F. No. 63, Division of Physics and Engineering, National Research Council of Canada, Ottawa.*

remembered that if full advantage had been taken of the possible increase in compression ratio, a probable gain in power of about 6% would have resulted.

Fuel B. Without alcohol this fuel was not capable of suppressing detonation at the 6 : 1 compression ratio, but with the 15% alcohol addition, this was overcome as is shown by the 1.2% increase in power at 750 r.p.m. and the gain of 3.4% at 450 r.p.m. As in the case of Fuel *A*, a slight increase in power might have been obtained by increasing the compression ratio for the alcohol–gasoline mixture.

The specific fuel consumption (Fig. 8) for the alcohol–gasoline mixture was practically the same as for the gasoline alone at 450 and at 750 r.p.m., while in the middle range it was 4–5% greater.

Fuel C. The gain in power of this fuel with 15% alcohol addition was 1.5% at 750 r.p.m. and 2.8% at 560 r.p.m. The curve was not taken to lower speeds, as a slight irregularity in the operation of the engine gave inaccurate results.

Specific fuel consumption increased for the alcohol–gasoline mixtures.

Gum

It was decided to subject the fuels, with their various blends to a copper dish "gum" test. The result of this test was as follows:

	Fuel *A*				Fuel *B*				Fuel *C*			
Sample number	1	2	3	4	5	6	7	8	9	10	11	12
"Gum" (mgm. per 100 cc.)	−2	−2	3	3	15	16	28	14	37	38	41	35

A certain amount of light corrosion was noted with the alcohol alone but no weighable amount of residue was found.

In all cases the gum content did increase slightly from the 100% gasoline to the 10% alcohol mixture, and dropped again with the 15% alcohol mixture. It is not thought that the alcohol had much effect on the gum, but it is interesting to note a similar rise and fall in each of the fuels tested.

The effect of storage was not considered, as the accelerated aging equipment has not yet been completed.

Ease-of-starting Test

Since much has been said about the difficulty of starting engines with fuels containing large quantities of alcohol, it was decided to try starting the engine on alcohol alone. The engine was run for a time on ethyl alcohol only, and then closed down for the night. The cooling water was allowed to circulate through the cylinder jacket, and the room temperature dropped to about 60° F. The next morning, with only alcohol in the fuel system, the engine was motored over at approximately 450 r.p.m. and began to fire in about 15 sec., showing little reluctance to starting. Several other starts were made in the same manner when the engine had been stopped for shorter periods.

Group 2

This section deals with tests which were similar to those in Group I, but in which the operating conditions were somewhat different.

Specific gravity at 60° F.	0.706	50% point	92.0° C.
Gum	0.4 mg. per 100 cc.	60% point	97.5° C.
Corrosive sulphur	Nil	70% point	103.5° C.
Total sulphur	0.002% by weight	80% point	111.0° C.
Initial boiling point	50° C.	90% point	122.5° C.
10% point	68° C.	End point	160.0° C.
20% point	74.5° C.	Recovery	99.0%
30% point	81.0° C.	Residue	0.9%
40% point	86.5° C.	Loss	00.1%

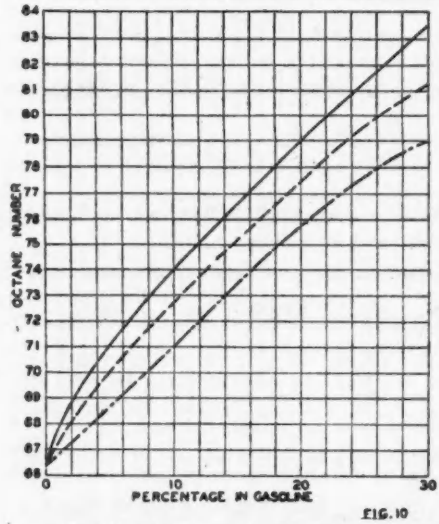


FIG. 10. *Octane number of gasoline with and without additions of ethyl and/or isopropyl alcohol.* ——— *Ethyl alcohol;* – – – – *ethyl and isopropyl alcohols;* — — — — *isopropyl alcohol.*

The gasoline which was used for a base fuel was a straight run, non-ethyl gasoline, with the above characteristics.

With this fuel were mixed various proportions of ethyl and/or isopropyl alcohol (See Table IV). The ethyl alcohol was 99.75% pure (by volume). The isopropyl alcohol contained 2.38%, by volume, of water.

Octane Number

The octane numbers were determined on the Series 30B engine under the C.F.R. Motor Method as described in the previous section, for gasoline alone, and for each of the alcohol–gasoline mixtures. The results are shown in Table IV and in Fig. 10.

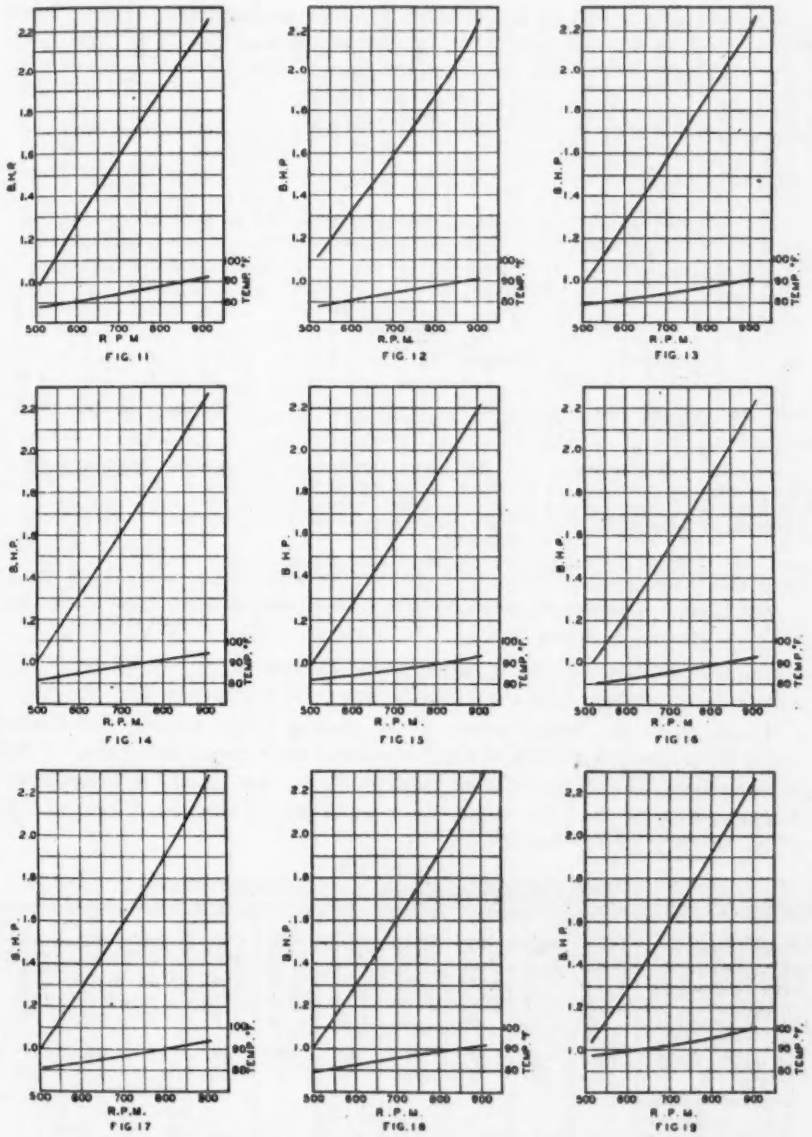
TABLE IV

INCREASE IN OCTANE NUMBER DUE TO ALCOHOL ADDITIONS

Sample No.	Gasoline, %	Ethyl alcohol, %	Isopropyl alcohol, %	Octane number C.F.R. Motor Method
13	100	0	0	66.4
14	90	10	0	74.0
15	80	20	0	79.0
16	70	30	0	83.5
17	90	5	5	72.8
18	80	10	10	77.5
19	70	15	15	80.3
20	90	0	10	71.0
21	80	0	20	75.75
22	70	0	30	79.0

Power and Consumption Curves

Power and consumption curves were found on the Armstrong Whitworth variable-compression engine.



FIGS. 11–19. *Power curves for gasoline only, gasoline-ethyl alcohol, gasoline-ethyl alcohol-isopropyl alcohol, and gasoline-isopropyl alcohol. Fig. 11 corresponds to Table V, Fig. 12 to Table VI, and so on to Fig. 19 which corresponds to Table XIV.*

The engine was thoroughly warmed and set at a compression ratio of 5.5 : 1 to permit the use of gasoline without detonation. The throttle was fully opened and the fuel mixture set as lean as possible without loss of power.

After running at 900 r.p.m. for three minutes, readings were taken. With the throttle in the full open position, the engine was slowed to 700 r.p.m. by means of the electrical dynamometer. Readings were taken again at the end of three minutes. This was repeated down to 500 r.p.m. and back again to 900 r.p.m. The same procedure was carried out for each blend and the power developed is shown in Figs. 11–20 and in Tables V–XIV.

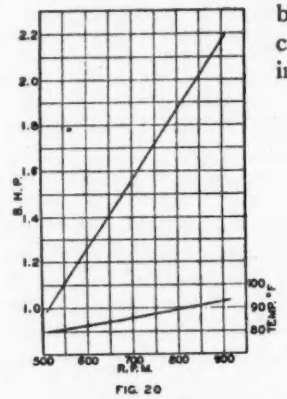


FIG. 20

FIG. 20. *Power curves for gasoline and isopropyl alcohol. This figure corresponds to Table XIV.*

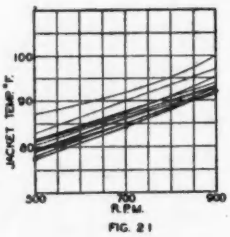


FIG. 21

FIG. 21. *Temperature of the cooling water at the outlet during determination of power curves.*

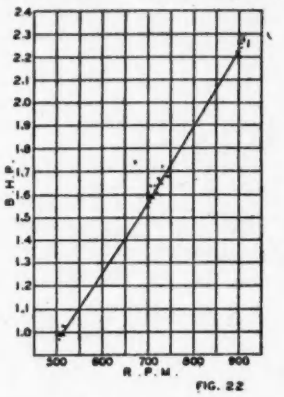


FIG. 22

FIG. 22. *Composite power curve—Fuels 13–22.*

The temperatures of the cylinder jacket cooling liquid are given. The cylinder head cooling, which is separate, was kept constant at 212° F.

Fig. 21 gives the temperatures of the cooling water leaving the engine during all of the power tests, the curve marked with circles being that of the gasoline alone. There is variation between curves due mainly to irregularity in temperature of the inlet water which could not be controlled, but all the curves are very similar in slope.

TABLE V

RESULTS OBTAINED WITH 100% GASOLINE

R.p.m. (actual)	915	920	710	710	500	510	720	720	905	900
Wt. supported, lb.	8.55	8.55	7.80	7.82	6.70	6.80	8.0	8.0	8.75	8.675
B.H.P. (observed)	2.24	2.25	1.58	1.59	.96	.99	1.64	1.64	2.26	2.23
Fuel, pt./hr.	1.78	1.78	1.70	1.70	1.60	1.62	1.70	1.70	1.77	1.76
Fuel, lb./B.H.P./hr.	.705	.702	.96	.95	1.48	1.46	.92	.92	.70	.70
Cyl. jacket, ° F.	95	94	88	87	83	78	81	84	88	91
Air inlet, ° F.	78	78	78	78	78	78	78	77.5	77.5	77.5
Pressure drop across ½-in. orifice on meter, in. of water	1.94	1.94	1.13	1.13	.56	.63	1.25	1.25	1.94	1.94

Pressure 760.4 mm.

TABLE VI

RESULTS OBTAINED WITH GASOLINE 90%, ETHYL ALCOHOL 10%

R.p.m. (actual)	910	905	710	712	505	520	720	725	900	900
Wt. supported, lb.	8.70	8.65	7.88	7.90	6.70	6.90	8.05	8.03	8.75	8.80
B.H.P. (observed)	2.26	2.24	1.60	1.61	0.97	1.03	1.66	1.66	2.25	2.26
Fuel, pt./hr.	1.97	1.97	1.88	1.88	1.78	1.78	1.87	1.85	1.91	1.92
Fuel, lb./B.H.P./ hr.	.78	.79	1.06	1.05	1.65	1.56	1.01	1.00	.76	.76
Cyl. jacket, ° F.	92	92	88.5	86	82	78	83	84.5	88	91
Air inlet, ° F.	78	78	78	78	78	77.5	77.5	77.5	77.5	77.5
Pressure drop across ½-in. orifice on meter, in. of water.	1.94	1.94	1.13	1.16	.59	.59	1.19	1.19	1.94	1.94

Pressure 760.4 mm.

TABLE VII

RESULTS OBTAINED WITH GASOLINE 80%, ETHYL ALCOHOL 20%

R.p.m. (actual)	910	900	705	705	500	500	720	720	905	910
Wt. supported, lb.	8.65	8.70	7.88	7.90	7.1	6.9	8.00	7.95	8.65	8.75
B.H.P. (observed)	2.25	2.24	1.59	1.59	1.01	0.99	1.65	1.64	2.24	2.28
Fuel, pt./hr.	1.98	1.97	1.89	1.88	1.78	1.77	1.86	1.86	1.92	1.92
Fuel, lb./B.H.P./ hr.	.80	.80	1.08	1.07	1.60	1.63	1.03	1.03	.78	.76
Cyl. jacket, ° F....	92	92.5	90	85	84	79	80.5	85	87	91
Air inlet, ° F.	78	78	77.5	77.5	77	77	77	77	77	77
Pressure drop across ½-in. orifice on meter, in. of water.	1.91	1.91	1.09	1.13	.56	.56	1.19	1.19	1.91	1.91

Pressure 760.4 mm.

TABLE VIII

RESULTS OBTAINED WITH GASOLINE 70%, ETHYL ALCOHOL 30%

R.p.m. (actual)	920	910	705	700	505	500	710	714	910	910
Wt. supported, lb.	8.80	8.75	8.0	8.05	7.15	7.0	8.05	8.05	8.6	8.75
B.H.P. (observed)	2.31	2.28	1.61	1.61	1.03	1.00	1.63	1.64	2.24	2.28
Fuel, pt./hr.	2.04	2.02	1.90	1.90	1.80	1.76	1.84	1.84	1.96	1.94
Fuel, lb./B.H.P./ hr.	.81	.82	1.08	1.08	1.61	1.62	1.04	1.03	.80	.78
Cyl. jacket, ° F.	96	96	95	89	88	81.5	84	88	88	93
Air inlet, ° F.	80	80	79.5	79.5	79.5	79	79	79	79	79
Pressure drop across ½-in. orifice on meter, in. of water	2	2	1.06	1.09	.56	.56	1.13	1.09	2	2

Pressure 771 mm.

TABLE IX

RESULTS OBTAINED WITH GASOLINE 90%, ETHYL ALCOHOL 5%, ISOPROPYL ALCOHOL 5%

R.p.m. (actual)	900	915	710	702	505	503	720	725	900	895
Wt. supported, lb.	8.5	8.5	7.9	7.85	6.9	6.9	7.9	8.0	8.7	8.7
B.H.P. (observed)	2.19	2.22	1.60	1.57	1.00	.99	1.63	1.66	2.24	2.22
Fuel, pt./hr.	1.83	1.84	1.73	1.74	1.62	1.62	1.72	1.72	1.80	1.79
Fuel, lb./B.H.P./ hr.	.75	.75	.97	1.00	1.45	1.47	.95	.93	.72	.73
Cyl. Jacket, ° F.	94	94	93	88	85	81.5	81	87	89	92
Air inlet, ° F.	78	78	78	78.5	78.5	78.5	79	79	79	79.5
Pressure drop across ½-in. orifice on meter, in. of water	1.94	1.97	1.13	1.13	.44	.44	1.25	1.22	1.94	1.91

Pressure 771 mm.

TABLE X

RESULTS OBTAINED WITH GASOLINE 80%, ETHYL ALCOHOL 10%, ISOPROPYL ALCOHOL 10%

R.p.m. (actual)	910	911	690	690	515	515	730	740	920	920
Wt. supported, lb.	8.6	8.6	7.6	7.6	6.8	6.8	7.7	7.95	8.55	8.65
B.H.P. (observed)	2.24	2.24	1.50	1.50	1.00	1.00	1.61	1.68	2.25	2.27
Fuel, pt./hr.	1.96	1.95	1.85	1.84	1.76	1.75	1.85	1.83	1.95	1.95
Fuel, lb./B.H.P./ hr.	.80	.79	1.12	1.12	1.60	1.59	1.04	.99	.79	.78
Cyl. jacket, ° F.	95	95	93	86.5	85	80	79	85	87	92
Air inlet, ° F.	78	78	78	78	78	78	78	78	78	78
Pressure drop across ½-in. orifice on meter, in. of water	2	2	1.06	1.06	.59	.63	1.28	1.31	2	2.03

Pressure 771 mm.

TABLE XI

RESULTS OBTAINED WITH GASOLINE 70%, ETHYL ALCOHOL 15%, ISOPROPYL ALCOHOL 15%

R.p.m. (actual)	915	905	704	704	505	503	702	703	910	910
Wt. supported, lb.	8.80	8.75	7.9	7.9	6.95	6.95	7.85	7.9	8.7	8.8
B.H.P. (observed)	2.30	2.26	1.59	1.59	1.00	1.00	1.57	1.59	2.26	2.29
Fuel, pt./hr.	1.97	1.97	1.88	1.88	1.78	1.77	1.83	1.84	1.97	1.97
Fuel, lb./B.H.P./ hr.	.79	.80	1.08	1.08	1.64	1.63	1.08	1.07	.80	.79
Cyl. jacket, ° F.	94	94	91.5	87	86.5	80.5	81	87	87	94
Air inlet, ° F.	78	78	78	78	78	78	78	78	78	78
Pressure drop across ½-in. orifice on meter, in. of water	2.03	2.03	1.13	1.13	.56	.56	1.16	1.16	1.97	2

Pressure 771 mm.

TABLE XII

RESULTS OBTAINED WITH GASOLINE 90%, ISOPROPYL ALCOHOL 10%

R.p.m. (actual)	910	915	703	700	495	500	720	730	910	905
Wt. supported, lb.	8.75	8.80	7.95	7.93	6.90	7.0	8.20	8.25	8.90	8.85
B.H.P. (observed)	2.28	2.30	1.60	1.59	.98	1.00	1.69	1.72	2.31	2.29
Fuel, pt./hr.	1.92	1.92	1.81	1.78	1.70	1.68	1.78	1.78	1.85	1.85
Fuel, lb./B.H.P./hr.	.756	.75	1.01	1.00	1.56	1.51	.94	.92	.72	.73
Cyl. jacket, ° F.	94	92	90	87	84	79	82	86	88	92
Air inlet, ° F.	78.5	78.5	78.5	78	78	78	78	78	78	78
Pressure drop across ½-in. orifice on meter, in. of water	2	2	1.13	1.13	.56	.56	1.25	1.25	2	2

Pressure 771 mm.

TABLE XIII

RESULTS OBTAINED WITH GASOLINE 80%, ISOPROPYL ALCOHOL 20%

R.p.m. (actual)	900	905	703	704	505	513	720	723	910	900
Wt. supported, lb.	8.75	8.80	7.90	7.90	6.95	7.05	8.08	8.10	8.80	8.83
B.H.P. (observed)	2.25	2.28	1.59	1.59	1.00	1.03	1.66	1.67	2.29	2.27
Fuel, pt./hr.	1.98	1.97	1.85	1.85	1.75	1.75	1.85	1.85	1.94	1.92
Fuel, lb./B.H.P./hr.	.80	.78	1.05	1.05	1.59	1.55	1.01	1.01	.77	.77
Cyl. jacket, ° F.	111	111	105	98	94	87	91	91	92.5	97
Air inlet, ° F.	77.5	78	78	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Pressure drop across ½-in. orifice on meter, in. of water	1.94	1.94	1.13	1.13	.56	.59	1.22	1.19	1.97	1.94

Pressure 770 mm.

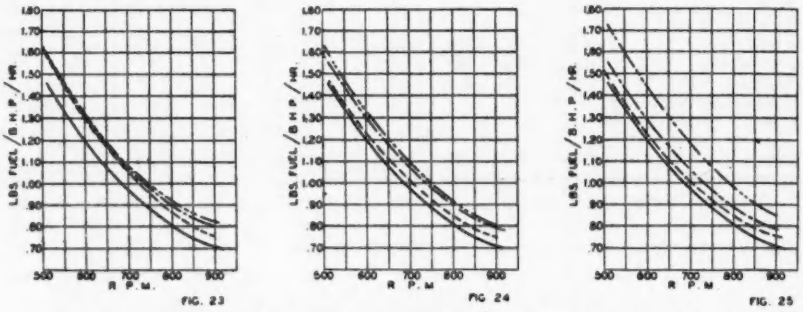
TABLE XIV

RESULTS OBTAINED WITH GASOLINE 70%, ISOPROPYL ALCOHOL 30%

R.p.m. (actual)	900	900	700	700	505	510	715	720	900	900
Wt. supported, lb.	8.60	8.60	7.85	7.75	6.90	6.80	7.75	7.85	8.50	8.58
B.H.P. (observed)	2.21	2.21	1.57	1.55	1.00	.99	1.58	1.61	2.19	2.21
Fuel, pt./hr.	2.07	2.06	1.98	1.98	1.87	1.86	1.95	1.97	2.04	2.02
Fuel, lb./B.H.P./hr.	.86	.85	1.16	1.18	1.72	1.73	1.13	1.12	.85	.84
Cyl. jacket, ° F.	94	94	92	87.5	86	80	82	85	87.5	93
Air inlet, ° F.	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Pressure drop across ½-in. orifice on meter, in. of water	1.91	1.91	1.06	1.06	.56	.56	1.13	1.13	1.91	1.91

Pressure 771 mm.

Fig. 22 is a composite power curve for all the samples and shows how little variation there is over the whole range. Figs. 23, 24 and 25 show the specific fuel consumption in lb./B.H.P./hr. For these consumptions, the specific gravities of the fuels were: gasoline 0.706, ethyl alcohol 0.789, isopropyl alcohol 0.789.



FIGS. 23, 24 and 25. *Specific fuel consumption for power curves obtained with Fuels 13–22. Fig. 23.* ——— *100% Gasoline;* – – – – *90% gasoline, 10% ethyl alcohol;* – – – – – *80% gasoline, 20% ethyl alcohol;* – – – – – *70% gasoline, 30% ethyl alcohol. Fig. 24.* ——— *100% Gasoline;* – – – – *90% gasoline, 5% ethyl alcohol, 5% isopropyl alcohol;* – – – – – *80% gasoline, 10% ethyl alcohol, 10% isopropyl alcohol;* – – – – *70% gasoline, 15% ethyl alcohol, 15% isopropyl alcohol. Fig 25.* ——— *100% Gasoline;* – – – – *90% gasoline, 10% isopropyl alcohol;* – – – – – *80% gasoline, 20% isopropyl alcohol;* – – – – *70% gasoline, 30% isopropyl alcohol.*

Highest Useful Compression Ratio (H.U.C.R.)

Tests were conducted on the Armstrong Whitworth variable-compression engine. It was intended to run accurate H.U.C.R. tests on all mixtures of fuel in this section, but when the fuel which remained was examined, it was found that there was not sufficient left to carry out the procedure as outlined in the H.U.C.R. tests in Group 1 and still attain stabilized engine conditions. It was decided however, to run these tests with a modified procedure as far as the quantity of fuel would permit, and with these explanations, the information in this section is offered for what it may be worth.

The engine was thoroughly warmed on gasoline and the H.U.C.R. for this fuel found under the following conditions:

Speed, 900 r.p.m.; full throttle power; spark advance, 12°; cylinder head cooling, 212° F.; cylinder wall cooling, 120°F.; leanest mixture for maximum power.

The variable-compression plug was screwed down, increasing the compression ratio, until the power developed passed a maximum and began to drop. This compression ratio was taken as the H.U.C.R. and was the point taken for starting the tests with the various mixtures of alcohol and gasoline. Fig. 26 and Table XV show the results of this test on the different fuels.

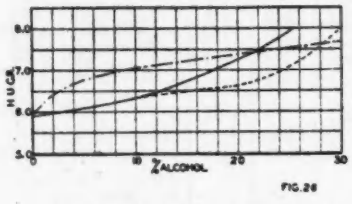


FIG. 26. *H.U.C.R. for Fuels 13–22.* ——— *Ethyl alcohol;* – – – – *isopropyl alcohol;* – – – – *ethyl and isopropyl alcohols.*

In addition to the H.U.C.R., the maximum power developed was noted, and these values are shown in Fig. 27. This power was the maximum power developed during the H.U.C.R. test and is incidental, as no attempt was made to attain maximum power other than by increasing the compression ratio.

TABLE XV

Gasoline, %	Ethyl alcohol, %	Isopropyl alcohol, %	Fuel No.	r.p.m.	Wt. lifted	B.H.P. obs. at actual r.p.m.	B.H.P. obs. at 900 r.p.m.	Pt./hr.	Fuel lb./ B.H.P./ hr.	Jacket temp., ° F.	H.U.C.R.
100	0	0	13	920	8.50	2.23	2.175	1.81	.728	121	5.9 : 1
90	10	0	14	920	8.7	2.29	2.22	1.97	.772	117	6.3 : 1
80	20	0	15	950	9.0	2.44	2.26	2.12	.791	115	7.25 : 1
70	30	0	16	950	9.2	2.50	2.315	2.19	.809	116	>8.0 : 1
90	5	5	17	930	8.65	2.30	2.195	2.01	.781	115	6.33 : 1
80	10	10	18	940	8.8	2.36	2.225	2.09	.809	119	6.62 : 1
70	15	15	19	955	9.2	2.51	2.305	2.15	.790	120	8.0 : 1
90	0	10	20	930	8.8	2.34	2.235	1.91	.736	119	7.05 : 1
80	0	20	21	945	8.9	2.40	2.245	2.05	.782	120	7.37 : 1
70	0	30	22	950	9.1	2.47	2.29	2.19	.818	120	7.65 : 1

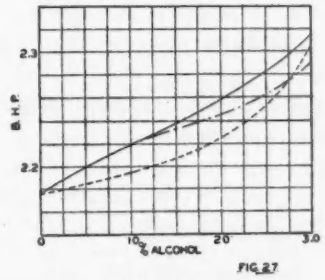


FIG. 27. *Maximum power noted during H.U.C.R. tests of Fuels 13–22.* ——— *Ethyl alcohol;* – – – – *ethyl and isopropyl alcohols;* – – – – *isopropyl alcohol.*

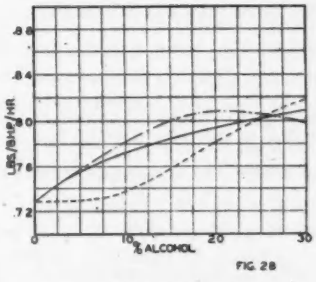


FIG. 28. *Specific fuel consumption noted during H.U.C.R. tests of Fuels 13–22.* ——— *Ethyl alcohol;* – – – – *ethyl and isopropyl alcohols;* – – – – *isopropyl alcohol.*

Normally, the test would be run with the engine speed constant at 900 r.p.m., but as the maximum rise in speed of 55 r.p.m. as the compression ratio was increased would affect the results but little, and as the fuel was limited, it was necessary to permit this rise in speed to occur. Specific fuel consumptions taken during this test are shown in Fig. 28.

Conclusions

In tests by the C.F.R. Motor Method the increase in anti-knock value with the addition of ethyl alcohol is greater than the increase due to the addition of isopropyl alcohol. Alcohol additions composed of one half ethyl alcohol

and the other half isopropyl alcohol, produced an increase in anti-knock value midway between those of additions consisting of the alcohols alone.

As the power–consumption tests were run under conditions which did not permit detonation, there was very little variation in the power curves. A composite power curve (Fig. 22) shows the power curve for gasoline without any alcohol (Sample No. 13) at the 500, 700 and 900 r.p.m. speeds. The power obtained for Samples 14–22 is shown by points. It will be noted that there is very little spreading of these points, which are within the accuracy of observation.

Temperatures in the cylinder jacket were fairly constant. While there was some slight variation, as shown in Fig. 21, this is largely due to temperature and pressure variation in the water supply, which could not be controlled.

Specific fuel consumptions were generally higher for alcohol–gasoline mixtures than for gasoline only. In the 10% alcohol mixtures, consumptions were higher when ethyl alcohol was used than when isopropyl alcohol was added. In the 20% mixtures the ethyl alcohol mixture consumptions were still somewhat higher than those of the isopropyl mixtures; but in the 30% mixtures, specific consumptions were higher for the isopropyl mixtures than for the ethyl alcohol mixtures.

In specific consumption, mixtures containing ethyl alcohol, isopropyl alcohol and gasoline fell between the mixtures containing either of the alcohols singly in the 30% mixture group. In mixtures with less than 30% alcohols the ethyl-isopropyl-gasoline has the lowest consumption.

Consumptions are given in lb./B.H.P./hr.

References

1. Bayley, C. H. and Hopkins, C. Y. Can. J. Research, 11 : 505—519. 1934.

2. Hopkins, C. Y. Preliminary report on the manufacture of grain alcohol for use in motor fuel. National Research Council Report. 1933.

WATER TOLERANCE OF MIXTURES OF GASOLINE WITH ETHYL ALCOHOL, ISOPROPYL ALCOHOL AND BENZENE[1]

By Colin H. Bayley[2] and Clarence Yardley Hopkins[3]

Abstract

The relation between water content and critical solution temperature of mixtures of gasoline with ethanol and isopropanol and with ethanol and benzene has been determined. Curves are presented which show the critical water contents of a wide range of mixtures at any temperature between +20° and −50° C. Three gasolines were used, two being straight-run and one a cracked gasoline. The mixtures contained 60 to 90% of gasoline with varying proportions of the other two components. Isopropanol has been found to bring about a marked increase in the critical water content of gasoline-ethanol mixtures to which it is added. Benzene is shown to be of little value for this purpose within the range of mixtures studied.

Introduction

The practice of using supplementary motor fuels in admixture with gasoline has increased steadily during the past few years. This trend is apparent chiefly in Europe among those countries which desire to be less dependent upon foreign sources of motor fuel. The gradual exhaustion of the world's petroleum deposits, which must be considered as inevitable, may be expected to result in the greater use of alternatives or substitutes for gasoline as it is now obtainable.

Owing to their availability, benzol and ethanol (ethyl alcohol) are in extensive use in the preparation of mixed motor fuels in which gasoline is the main constituent. Recent developments make it appear that isopropanol (isopropyl alcohol) can be manufactured cheaply from waste gases which are by-products of the petroleum industry, and it is not unlikely that in the near future this substance may become commercially available as a fuel.

A problem arises in connection with the use of mixed fuels containing ethanol, namely, the possibility of separation into two liquid phases upon the addition of relatively small amounts of water. At a given temperature any alcohol-gasoline mixture has a critical water content and conversely, any such mixture containing dissolved water has a critical solution temperature or "cloud" temperature below which separation into two phases will occur. This is of special practical importance in considering the feasibility of using blended fuels in countries in which low temperatures are encountered in winter.

Ternary mixtures of gasoline, ethanol and isopropanol were studied by Rothen and Boutier (7). Isopropanol was added to various mixtures of

[1] *Manuscript received June 14, 1934.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Chemist, National Research Laboratories, Ottawa.*

[3] *Chemist, National Research Laboratories, Ottawa.*

gasoline with 96% ethanol* until homogeneous solutions were obtained. The range of critical solution temperatures investigated was +16° to −18° C. Whilst Rothen and Boutier do not describe the properties of the isopropanol, their results indicate that it contained several per cent of water.

Rothen and Boutier also examined mixtures in which the third component was benzol, but found that it was of little value in lowering the critical solution temperature.

Ternary mixtures of gasoline, benzol and ethanol have been studied by Legrand (5) who determined the critical solution temperatures of mixtures containing denatured 95% alcohol. A number of gasoline-ethanol-benzol mixtures were examined by Spausta (8) who determined the water tolerance at 20° C.

The cloud temperatures of a few mixtures of gasoline, ethanol and benzol with small amounts of water were determined by Swietoslawski, Pfanhauser and Bakowski (9). The critical solution temperatures were found to range from −22.5° C. to −75° C.

Baron, Boulanger and LeGrain (1) determined the cloud temperatures of a series of twelve mixtures of aviation gasoline, "motor benzole" and 99% ethanol.

King and Manning (4) investigated ternary mixtures containing benzol as the third component, the temperature range studied being −10° to +20° C. The limits of miscibility at these temperatures for mixtures prepared from alcohols of 94 to 98% strength (by volume) are shown on ternary diagrams.

Ormandy, Pond and Davies (6) determined the water tolerance of a long series of mixtures of gasoline and aliphatic alcohols at one temperature, *viz.*, 15° C.

The present investigation deals with the determination of the critical solution temperatures of mixtures of *(a)* gasoline and isopropanol, and *(b)* gasoline and benzene with ethanol containing known amounts of water. From these results, curves are constructed showing the critical water content for a wide range of ternary mixtures of the above substances.

Materials

Gasoline

The properties of the three gasolines used in this investigation are given in Table I. Gasolines *A* and *B* were commercial aviation gasolines, gasoline *C* was a regular grade automobile fuel. None of these gasolines contained tetraethyl lead.

Ethanol

A series of solutions of ethanol and water were prepared from commercial absolute alcohol. The water content of each solution was checked by density determinations. The data are given in Table II.

**i.e., various mixtures of gasoline with ethanol, the ethanol containing 96% of ethyl alcohol.*

TABLE I

PROPERTIES OF GASOLINES USED

	A	*B*	*C*
Type	Straight run aviation	Straight run aviation	Liquid phase cracked
Density $d_{15.6}^{15.6}$	0.738	0.715	0.728
Gum (mg./100 cc.)	0.4	0.4	16.0
Sulphur %	0.002	0.002	0.003
A.S.T.M. Distillation			
I.B.P. °C.	72	26	35
10%	91	68	55
20	96	74.5	69.5
30	101	81	84
40	106	86.5	99
50	110	92	112
60	115	97.5	124.5
70	120	103.5	138.5
80	127.5	111	155
90	139.5	122.5	163
End point	171.5	160	196
Recovery %	98	99	96
Residue %	1.3	0.9	1.6
Loss %	0.7	0·1	2.4

TABLE II

WATER CONTENT OF ETHANOL USED

No.	Alcohol, % by weight	Water, % by vol.*	No.	Alcohol, % by weight	Water, % by vol.*
1	93.03	5.65	6	96.62	2.69
2	93.99	4.85	7	96.71	2.62
3	95.08	3.97	8	97.18	2.25
4	96.00	3.20	9	97.78	1.69
5	96.23	3.01	10	97.96	1.63

* *Temperature, 15.6° C.*

Isopropanol

Two grades of isopropanol obtained respectively from the Eastman Kodak Company and from Schuchardt were used. Their properties are given in Table III.

TABLE III

PROPERTIES OF ISOPROPANOL USED

Alcohol	d_4^{20}	B.p. at 760 mm. Hg.	% water by vol.	d_4^{20} after dehydration	B.p. at 760 mm. Hg. after dehydration, °C.
A (E.K.)	0.7927	80.4	2.38	0.7854	82.4
B (S)	0.7865	81.8	0.80	0.7855	82.4

Since the constants for the dehydrated alcohols are those of pure isopropanol, it follows that water was the only impurity present in the original materials. The identity of the dehydrated products was further shown by the fact that mixtures of gasoline and ethanol with the same volume of either of the above alcohols showed critical solution temperatures which did not vary by more than 1° C. The same was true if the alcohols were used before dehydration, provided that their respective water contents were taken into account when computing the total water content of the gasoline-ethanol-isopropanol mixture.

Benzene

Schuchardt's benzene "for molecular weight determination" was used. Since it showed no turbidity at −50° C., the water content may be taken as less than 0.01%, according to the extrapolated data of Groschuff (3). This quantity of water may be neglected for the purposes of the present investigation.

Experimental

The apparatus used consisted of a 6 × $\frac{5}{8}$-in. test tube fitted with a stopper carrying a thermometer and stirrer. This tube was supported in a larger tube which served as an air-chamber, the assembly being immersed in a mixture of acetone and carbon dioxide snow contained in a Dewar flask.

In making an experiment, about 10 cc. of the mixture was placed in the inner tube and cooled with continual stirring until the cloud point was reached. The assembly was then removed from the Dewar while the temperature of the mixture rose slowly, the stirring being continued. The point at which the cloud suddenly disappeared was taken as the critical solution temperature. The results of several determinations showed that the temperatures of appearance and disappearance of the cloud were identical. Repeated determinations with the same mixture gave identical readings for the cloud temperature, showing that there was no absorption of moisture by the mixture under the conditions of the experiment.

The calculation of the critical water contents has been based on the sum of the volumes of the components before mixing. This method neglects the change in volume on mixing gasoline and ethanol, but this change is sufficiently small to be neglected in the present experiments.

With mixtures containing gasoline, ethanol and benzene, the cloud point is more difficult to detect than when benzene is absent, and becomes still more obscure as the ratio of benzene to alcohol is increased. In the latter case, the cloud is very faint and breaks up into tiny droplets when the solution is cooled a few degrees below the cloud temperature. The cloud points of mixtures made with cracked gasoline were more difficult to determine than those containing straight run gasoline. The initial cloud in the former is little more than a bluish opalescence. This is especially true of mixtures in which the content of alcohol is less than 10%.

Frequent check determinations made with freshly prepared mixtures gave results agreeing to within 0.5° C. Temperatures were read to 0.5° C. and are recorded to the nearest degree. On account of the variable composition of gasoline it is to be expected that no two gasolines when mixed with equal volumes of alcohol would give mixtures having exactly the same critical solution temperatures. The results of Bridgeman and Querfeld (2) show that two gasolines having almost identical densities and distillation ranges gave mixtures whose cloud points differed by more than 2° C. For this reason it was felt that nothing was to be gained by recording temperatures to a fraction of a degree.

A. Gasoline-Ethanol

The critical solution temperatures of mixtures of gasolines *A* and *C* with ethanol containing various percentages of water are shown in Figs. 1 and 2.

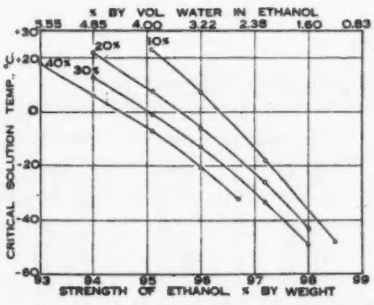


FIG. 1. *Critical solution temperatures of mixtures of gasoline C with ethanols of various strengths.*

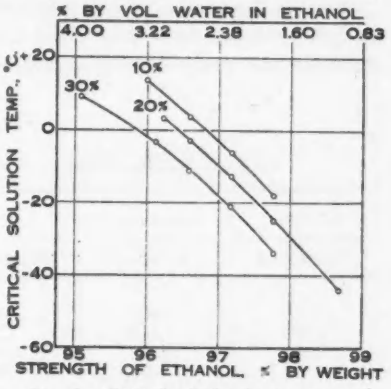


FIG. 2. *Critical solution temperatures of mixtures of gasoline A with ethanols of various strengths.*

B. Gasoline-Ethanol-Isopropanol

The critical solution temperatures of mixtures of gasoline, ethanol and isopropanol *A* containing 90% by volume of gasoline *A* are given in Fig. 3.

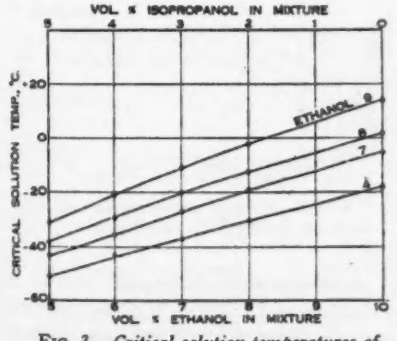


FIG. 3. *Critical solution temperatures of mixtures containing 90% gasoline A.*

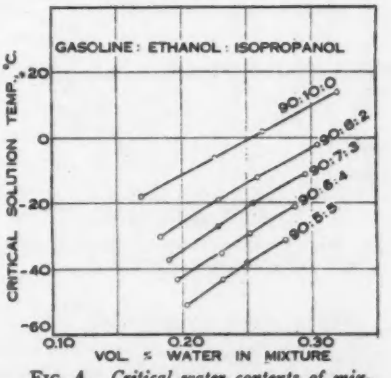


FIG. 4. *Critical water contents of mixtures containing 90% gasoline A.*

Four ethanol-water mixtures containing progressively less water were used in this series of experiments. The effect of water content is shown more clearly in Fig. 4 in which the water content, expressed as a percentage of the total mixture is plotted against critical solution temperature for various mixtures containing 90% of gasoline together with various proportions of ethanol and isopropanol.

It will be seen that for a given total water content of the mixture there is a slight though regular increase in the extent to which the critical solution temperature is lowered when the ethyl alcohol in the mixture is progressively replaced by isopropanol.

The increase in the critical water content of the mixture occasioned by increasing the percentage of isopropanol at the expense of the ethanol is shown in Table IV, in which the critical water contents of the first four of the above mixtures are compared for temperatures of 0°, −20° and −40° C.

TABLE IV

CRITICAL WATER CONTENTS OF MIXTURES CONTAINING 90% GASOLINE *A*

Mixture			Critical water content, % by vol.		
Gasoline *A*	Ethanol	Isopropanol	0° C.	−20° C.	−40° C.
90	10	0	0.25	0.16	0.07
90	8	2	0.31	0.22	0.15
90	7	3	0.35	0.26	0.18
90	6	4	0.38	0.29	0.21

Figs. 5 and 6 give the results of similar experiments carried out with mixtures containing 80 and 70% of gasoline *A* respectively.

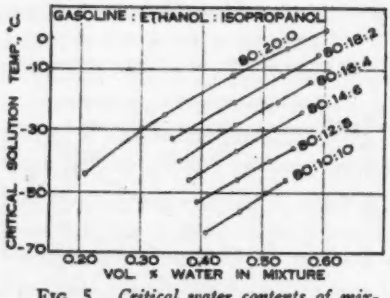


FIG. 5. *Critical water contents of mixtures containing 80% gasoline A.*

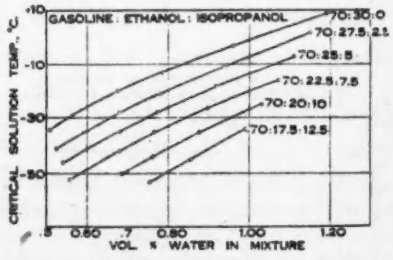


FIG. 6. *Critical water contents of mixtures containing 70% gasoline A.*

For a given temperature the critical water content increases rapidly as the percentage of gasoline in the mixture is decreased. Table V gives the critical water content of these mixtures for temperatures of 0°, −20° and −40° C.

TABLE V

CRITICAL WATER CONTENTS OF MIXTURES CONTAINING 80 AND 70% GASOLINE *A*

Mixture			Critical water content, % by vol.		
Gasoline, %	Ethanol, %	Isopropanol, %	0° C.	−20° C.	−40° C.
80	20	0	0.57	0.38	0.24
80	16	4	0.72	0.53	0.37
80	12	8	0.92	0.71	0.51
70	30	0	1.02	0.68	0.45
70	25	5	1.26	0.89	0.62
70	20	10	1.50	1.11	0.82

Similar experiments were carried out using straight run gasoline *B* which possessed a higher volatility than gasoline *A*. It was found that for a given water content, the critical solution temperatures were lower for mixtures made up from the straight run gasoline having the higher volatility. The results are given in Table VI.

TABLE VI

CRITICAL SOLUTION TEMPERATURES OF MIXTURES CONTAINING 90, 80 AND 70% OF GASOLINE *B* AND VARIOUS PERCENTAGES OF ETHANOL

Mixture			Water content of mixture, % by vol.	Critical solution temp., ° C.
Gasoline, %	Ethanol, %	Isopropanol, %		
90	10	0	0.23	−12
90	9	1	0 23	−18
90	8	2	0.23	−26
90	7	3	0.23	−33
80	20	0	0.45	−21
80	18	2	0.45	−29
80	16	4	0.46	−36
80	14	6	0.46	−44
70	30	0	0.68	−29
70	27.5	2.5	0.67	−35
70	25	5	0.66	−42
70	22.5	7.5	0.65	−49

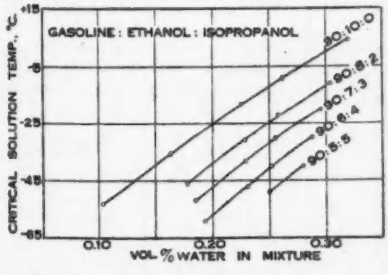


FIG. 7. *Critical water contents of mixtures containing 90% gasoline C.*

Figs. 7, 8 and 9 give the results obtained with mixtures of cracked gasoline *C* with ethanol and isopropanol. As before, the mixtures investigated contained 90, 80 and 70% of gasoline respectively.

It will be seen that the critical water contents of these mixtures are higher

than those of mixtures containing either of the straight run gasolines. This is shown in Table VII by comparison with the results given in Tables IV and V.

TABLE VII

CRITICAL WATER CONTENTS OF MIXTURES CONTAINING 90, 80 AND 70% GASOLINE *C*

Mixture			Critical water content, % by vol.		
Gasoline *C*, %	Ethanol, %	Isopropanol, %	0° C.	−20° C.	−40° C.
90	10	0	0.30	0.22	0.15
90	8	2	0.35	0.27	0.19
90	7	3	0.38	0.30	0.22
90	6	4	0.41	0.33	0.25
80	20	0	0.70	0.50	0.35
80	16	4	—	0.64	0.46
80	12	8	—	0.80	0.60
70	30	0	1.25	0.84	0.59
70	25	5	—	1.09	0.76
70	20	10	—	1.25	1.00

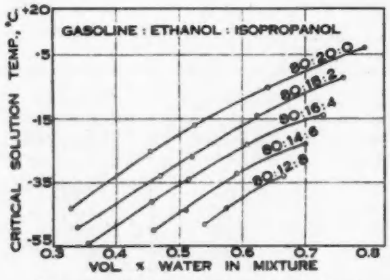


FIG. 8. *Critical water contents of mixtures containing 80% gasoline C.*

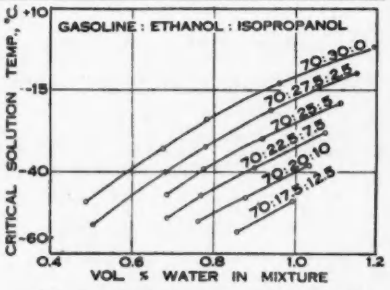


FIG. 9. *Critical water contents of mixtures containing 70% gasoline C.*

A comparison of the critical solution temperatures obtained with straight run gasoline *A* and cracked gasoline *C* is given in Table VIII.

TABLE VIII

COMPARISON OF CRITCAL SOLUTION TEMPERATURES OF STRAIGHT RUN AND CRACKED GASOLINE WITH ETHANOL NO. 8

Mixture			Critical solution temp., ° C.	
Gasoline, %	Ethanol, %	Isopropanol, %	Straight run (*A*)	Cracked (*C*)
90	10	0	− 6	−18
90	8	2	−19	−31
90	5	5	−43	Below −55
80	20	0	−12	−25
80	16	4	−28	−41
80	12	8	−46	Below −55
70	30	0	−20	−33
70	25	5	−35	−47
70	20	10	−50	Below −55

C. Gasoline, Ethanol and Benzene

Gasoline *C* was used in most of the mixtures with ethanol and benzene. The critical solution temperatures for mixtures containing 80% of gasoline C are shown in Fig. 10. Fig. 11 gives the critical water content of four such mixtures at temperatures corresponding to winter conditions. It is evident that the higher the ratio of alcohol to benzene the greater is the critical water content.

Figs. 12, 13 and 14 show the same results for mixtures containing 90, 70 and 60% of gasoline.

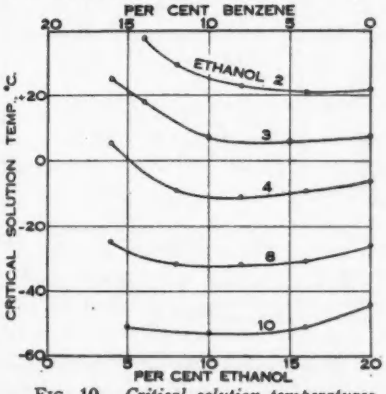


FIG. 10. *Critical solution temperatures of mixtures containing 80% gasoline C.*

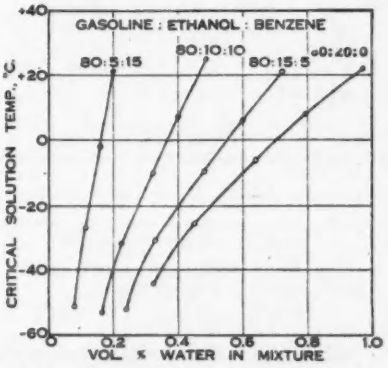


FIG. 11. *Critical water contents of mixtures containing 80% gasoline C.*

Mixtures of gasoline and benzene containing 30 or 40% of the latter deposit crystals at temperatures only slightly below 0° C. The addition of ethanol lowers the crystallizing temperature and if sufficient alcohol is present (depending on the water content), the mixture may develop a cloud before crystallization occurs. The crystallization point is lowered when commercial benzol is used in place of pure benzene as shown in Table XIII.

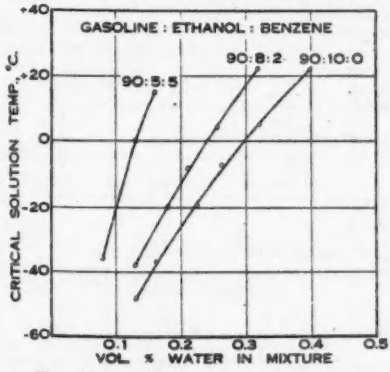


FIG. 12. *Critical water contents of mixtures containing 90% gasoline C.*

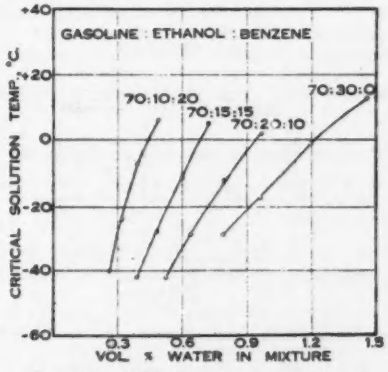


FIG. 13. *Critical water contents of mixtures containing 70% gasoline C.*

With ternary mixtures containing not less than 70% of cracked gasoline, crystallization is not a factor in the temperature range examined. Mixtures having 60% of gasoline and more than 15% of benzene (with ethanol) would be expected to show crystallization when exposed to severe winter temperatures (Fig. 14).

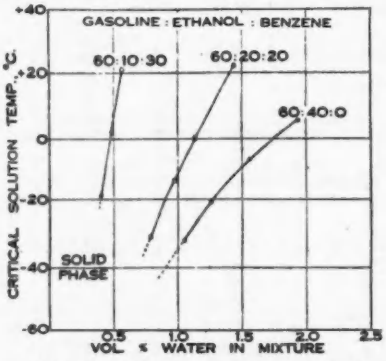


FIG. 14. *Critical water contents of mixtures containing 60% gasoline C.*

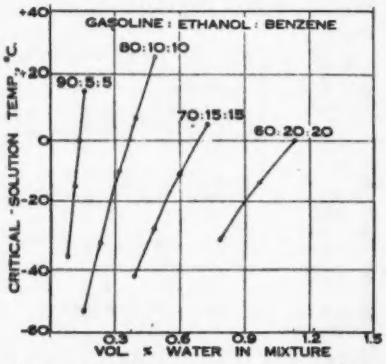


FIG. 15. *Critical water contents of mixtures with gasoline C in which the ratio of alcohol to benzene is 1 : 1.*

When the ratio of alcohol to benzene is kept constant at 1 : 1, the critical water content increases rapidly with decreasing percentages of gasoline (Fig. 15).

The effect of varying two components at a time while keeping the third constant may be considered as follows:—

(a) If the proportion of alcohol to total mixture is constant and the percentage of benzene is increased, the critical water content is increased only moderately as shown in Tables IX and X.

TABLE IX

CRITICAL WATER CONTENT OF MIXTURES CONTAINING 10% OF ALCOHOL

Mixture			Critical water content, % by vol.		
Gasoline *C*, %	Alcohol, %	Benzene, %	0° C.	−20° C.	−40° C.
90	10	0	0.30	0.22	0.15
80	10	10	0.36	0.28	0.20
70	10	20	0.43	0.34	0.26
60	10	30	0.48	0.40	Cryst.

TABLE X

CRITICAL WATER CONTENT OF MIXTURES CONTAINING 20% OF ALCOHOL

Mixture			Critical water content, % by vol.		
Gasoline *C*, %	Alcohol, %	Benzene, %	0° C.	−20° C.	−40° C.
80	20	0	0.70	0.50	0.35
70	20	10	0.94	0.72	0.54
60	20	20	1.12	0.90	—

(b) On the other hand, with mixtures containing a fixed percentage of benzene, the critical water content increases rapidly with increasing percentage of alcohol as shown by Table XI and Fig. 16.

TABLE XI

CRITICAL WATER CONTENTS OF MIXTURES CONTAINING 10% OF BENZENE

Mixture			Critical water content, % by vol.		
Gasoline *C*, %	Alcohol, %	Benzene, %	0° C.	−20° C.	−40° C.
90	—	10	—	—	—
80	10	10	0.36	0.28	0.20
70	20	10	0.94	0.72	0.54
60	30	10	1.52	1.24	—

(c) When the proportion of gasoline to total mixture is constant, the maximum water tolerance would be obtained by using "absolute"* alcohol for the remainder of the mixture and leaving out the benzene entirely (Figs. 11, 12, 13 and 14). The situation is different when the alcohol available for mixing contains water, since the replacement of part of the moist alcohol by dry benzene reduces the water content of the final mixture. Although the critical water content is lowered at the same time, the first effect may more than compensate for the second. For example, a mixture containing 60% of gasoline *C* and 40% of alcohol No. 2 has a critical solution temperature of +6° C. If 20% of the alcohol is replaced by benzene, the critical solution temperature becomes −14° C., a lowering of 20°. The respective water contents and critical solution temperatures are shown in Table XII.

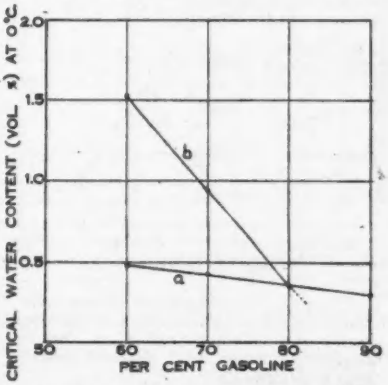


FIG. 16. *Critical water contents at 0° C. of ternary mixtures containing (a) 10% alcohol, and (b) 10% benzene.*

TABLE XII

USE OF BENZENE TO INCREASE WATER TOLERANCE

Mixture			Water content, % by vol.	Critical sol. temp., ° C.	Critical water content at 0° C., % by vol.	Water tolerance at 0° C., % by vol.
Gasoline *C*, %	Alcohol, No. 2, %	Benzene, %				
60	40	0	1.92	+ 6	1.76	—
60	20	20	0.96	−14	1.12	0.16

**Alcohol containing no water.*

When the percentage of gasoline to be used in the mixture and the water content of the alcohol are fixed, there is a definite percentage of benzene which will give maximum water tolerance. This can be found by plotting the actual water contents of possible mixtures against percentage of benzene, as has been done in Fig. 17. The water tolerance of a mixture at a given temperature is defined as the difference between its actual water content and the critical water content at that temperature.

It is readily seen that a mixture containing approximately 10% of benzene will have a greater water tolerance at 0° C. than any other mixture made with 95% (by weight) alcohol* and containing 70% of gasoline *C*. However,

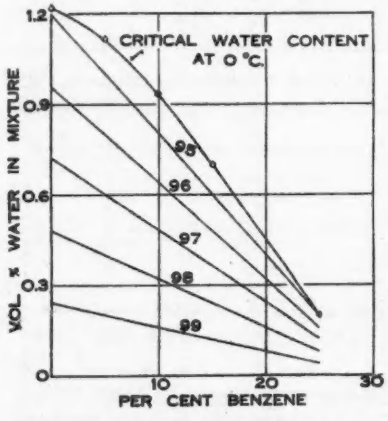


FIG. 17. *Relation between critical water content and actual water content of mixtures made with alcohol containing varying amounts of water. All mixtures contain 70% of gasoline C.*

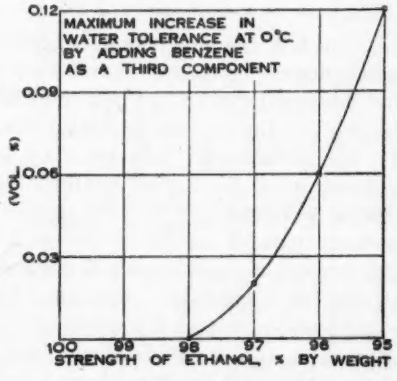


FIG. 18. *Constructed from Fig. 17 to show limited value of benzene for increasing water tolerance. Mixtures contain 70% gasoline C.*

the increase in water tolerance which can be secured by introducing benzene as a third component becomes rapidly less when drier alcohol is used. Ultimately, as shown in Fig. 18, a point is reached at which no increase in the water tolerance is possible, and for the particular conditions stated, the limit is reached when alcohol of approximately 98% strength (by weight) is used. With mixtures containing 60 and 80% of gasoline respectively, a similar limit is observed with alcohol of a strength of between 97 and 98%.

If a mixture containing 90% of gasoline is desired, it appears that the remainder of the mixture may consist entirely of moist alcohol, since the introduction of benzene into the formula gives a negligible increase in water tolerance. Even in those mixtures based on 60, 70 and 80% gasoline, the increase in water tolerance to be obtained by using benzene is small in comparison with that attainable by using alcohol containing 1% less of water.

**See footnote p. 506.*

With gasoline *C* and alcohol No. 4, the critical solution temperatures of mixtures containing commercial benzol are about 3° C. higher than when pure benzene is used, as shown in Table XIII.

TABLE XIII

COMPARISON OF PURE BENZOL AND COMMERCIAL BENZOL

Mixture			Critical solution temp., ° C.	
Gasoline *C*, %	Alcohol No. 4, %	Benzene or benzol, %	Pure benzene	Commercial benzol
90	5	5	+15	+17
80	10	10	−10	− 7
70	15	15	−28	−25
60	20	20	Cryst.	−45
75	10	15	−18	−15

The difference between the critical solution temperatures of mixtures of straight run gasoline *B* and of cracked gasoline *C* is given in Table XIV for alcohols of two strengths.

TABLE XIV

COMPARISON OF STRAIGHT RUN AND CRACKED GASOLINE

Mixture				Critical solution temp., ° C.	
Strength of alcohol (% by wt.)	Gasoline	Alcohol	Benzene	Straight run (*B*)	Cracked (*C*)
96.00	80	20	0	− 1.5	− 6
96.00	80	16	4	− 5	− 9
96.00	80	12	8	− 7	−11
96.00	80	8	12	− 4	− 9
95.08	80	20	0	+12	+ 8
95.08	80	15	5	+10	+ 6
95.08	80	10	10	+11	+ 7
95.08	80	6	14	+22	+18
96.00	90	5	5	+18	+15
96.00	80	10	10	− 5.5	−10
96.00	70	15	15	−25	−28
96.00	60	20	20	Cryst.	Cryst.

(D) Comparison of Isopropanol and Benzene as the Third Component in Gasoline–Ethanol Mixtures

The effectiveness of isopropanol in lowering the critical solution temperature of any given mixture is far greater than that of benzene (Table XV).

TABLE XV

CRITICAL SOLUTION TEMPERATURES OF 90 : 5 : 5 MIXTURES HAVING BENZENE OR ISOPROPANOL AS THE THIRD COMPONENT, GASOLINE *C*

No.	Ethanol strength, % by wt.	Critical solution temp., ° C.	
		Benzene	Isopropanol
4	96.00	+15	Below −55
5	96.71	0	Below −55
6	97.18	−15	Below −55

This is further illustrated in Table XVI which includes mixtures containing 80 and 90% of gasoline respectively. In the latter case, the use of benzene as the third component actually raises the critical solution temperature, whereas isopropanol lowers it by more than 50° C.

The critical water contents of various mixtures of gasoline *C* and ethanol together with benzene or with isopropanol are compared in Table XVII.

TABLE XVI

CRITICAL SOLUTION TEMPERATURES OF VARIOUS MIXTURES

Mixture				Critical solution temp., ° C.
Gasoline *C*	Ethanol 4	Third component		
80	20	None		− 6
80	10	Comml. benzol	10	− 7
80	10	C.p. benzene	10	−10
80	10	Isopropanol *A*	10	Below −55
80	10	Isopropanol *B*	10	Below −55
90	10	None		+ 7.5
90	5	Comml. benzol	5	+17
90	5	C.p. benzene	5	+15
90	5	Isopropanol *A*	5	−40
90	5	Isopropanol *B*	5	Below −55

The advantage of isopropanol in increasing the critical water content is clearly shown.

TABLE XVII

CRITICAL WATER CONTENTS OF VARIOUS MIXTURES

Mixture				Critical water content (% by volume)		
Gasoline *C*	Ethanol	Third component		0° C.	−20° C.	−40° C.
90	10	None		0.30	0.22	0.15
90	5	Benzene	5	0.14	0.10	0.07
90	5	Isopropanol	5	>0.45	>0.35	0.28
80	20	None		0.70	0.50	0.35
80	10	Benzene	10	0.36	0.28	0.20
80	10	Isopropanol	10		>0.83	>0.65
70	30	None		1.25	0.84	0.59
70	20	Benzene	10	0.94	0.72	0.53
70	20	Isopropanol	10	>1.6	>1.3	1.00

Discussion

Absolute ethanol and gasoline mix in all proportions, and mixtures containing 10 to 40% of absolute alcohol are stable at temperatures down to −60° C. or lower. Nevertheless, the addition of a small percentage of water to these mixtures will cause separation into two phases. The critical water content is small at low temperatures and for mixtures containing from 10 to 40% alcohol it varies from 0.1 to 1.0% by volume at −40° C.

The water tolerance of a given ethanol-gasoline mixture can be raised by the addition of a third liquid or "blending agent," and it has been thought that this practice would be desirable in countries where sub-zero temperatures prevail during the winter.

An ideal blending agent should be cheap, effective and available in large quantities. Acetone, ethyl ether and *n*-butanol are considered to be too costly for this purpose. The remaining possibilities appear to be benzene from coal carbonization, and isopropanol, which is being produced at present from waste gases at petroleum refineries.

Benzene may be used to increase moderately the critical water content of ethanol-gasoline mixtures by substituting benzene for part of the gasoline. If the alcohol is of a strength less than 97 or 98% by weight, a slight increase in water tolerance may be obtained by replacing part of the alcohol in the formula by benzene. This is true only if the mixture contains less than 90% of gasoline. The existence of optimal ratios of benzene to ethanol for maximum water tolerance has been demonstrated. While benzene has other properties which make it desirable as a component of mixed motor fuels, its effect in increasing water tolerance appears to be too slight to be of practical value.

On the other hand, isopropanol increases the water tolerance and the critical water content of any ethanol-gasoline mixture to which it is added. If half of the ethanol in a given formula is replaced by isopropanol, the critical water content at −20° C. is increased by about 60%, while at −40° C. it is nearly doubled. Although there is no information available as to the degree of water tolerance desirable in mixed motor fuels, the results given above indicate that mixtures of reasonably high water tolerance may be prepared by the addition of isopropanol to ethanol-gasoline blends.

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HYDROTHERMAL SYNTHESIS OF CALCIUM HYDROSILICATES[1]

By V. A. Vigfusson,[2] G. N. Bates[3] and T. Thorvaldson[4]

Abstract

A crystalline substance which appears in steam-cured Portland cement mortar has been shown to be a calcium hydrosilicate and has been prepared by hydrothermal synthesis from mixtures of silica sand with lime, dicalcium silicate and tricalcium silicate, silica gel and lime (after preliminary steam treatment and ignition) and by the action of saturated lime water on quartz crystals or fused silica plates. The crystals appear not to be acted on by solutions of sodium sulphate, calcium sulphate or alkali hydroxides, but they are slowly decomposed by solutions of magnesium sulphate and alkali carbonates and rapidly by dilute acids and ammonium salts. The crystals were obtained free from amorphous matter by growing them on quartz or silica plates in saturated lime water. When the compound was prepared in this way, the lime-silica-water ratio was found to be 2 : 1 : 1, the formula being therefore $2CaO.SiO_2.H_2O$ or $H_2Ca_2SiO_4$. This product usually appears as thin lath-like prisms showing parallel extinction, positive elongation and moderate birefringence. The crystals are optically positive with a fairly large optic angle. $2V = 68°$. The indices of refraction are $\alpha_{Na} = 1.614 \pm .002$, $\beta_{Na} = 1.620 \pm .002$, $\gamma_{Na} = 1.633 \pm .002$. The optical plane is parallel to the macropinacoid (100) and the acute bisectrix Z is parallel to the direction of elongation which is taken as the crystallographic axis C. The optical properties and X-ray pattern are distinctive and entirely different from those of hillebrandite or foshagite, which have the same composition.

Another crystalline calcium hydrosilicate was obtained by hydrothermal synthesis from excess lime and silica gel. This appeared as very small needle-like prisms, observable only when magnified about 200 times. The crystals show parallel extinction, positive elongation and very low birefringence with an index of refraction of $1.597 \pm .003$. Analysis of this product, extracted with a glycerol-water mixture to remove excess lime, gave a lime-silica ratio of 2 to 1 with an uncertain amount of water of at least one mole. The X-ray pattern is distinctive and shows only slight similarity to the hillebrandite pattern.

Introduction

A preliminary paper (11) described a crystalline substance formed in Portland cement mortar subjected to the action of saturated steam under pressure. Mortars thus treated show an increased resistance to the disintegrating action of sulphate solutions. This effect varies with the temperature and duration of the steam treatment (12, 13) and for a given cement appears to be related to the amount of the observed crystalline product formed. When a Portland cement mortar, made with quartz sand and a cement high in tricalcium silicate, is subjected to the action of saturated steam at say 150° C. and the product examined by the microscope, hexagonal plates of calcium hydroxide are soon observed in the mortar, the amount of these increasing with continued treatment. There is observed in addition the presence of birefringent crystals in the form of thin lath-like plates which increase in number and size as the treatment progresses, while the amount of the hexa-

[1] *Manuscript received July 10, 1934.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon Canada, with financial assistance from the National Research Council of Canada.
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gonal plates of calcium hydroxide reaches a maximum and then decreases until they disappear completely. The optical properties of the lath-like plates could not be identified with those of any previously described product.

Preliminary Experiments

Attempts to separate these crystals completely by mechanical means from the cement mortar in which they were embedded were not successful. It was, however, possible to study the action of other substances on the product by means of the microscope, without obtaining a pure sample. The crystals were apparently not attacked by solutions of calcium sulphate or sodium sulphate, but were slowly decomposed by solutions of magnesium sulphate, behaving in these respects similarly to steam-cured Portland cement mortars (13). The crystals were found to be quite stable in solutions of sodium, potassium and ammonium hydroxides, but were readily decomposed by dilute acids and by solutions of ammonium salts. They were slowly decomposed by solutions of normal alkali carbonates with the formation of calcite crystals on the surfaces attacked. Further, with dilute sulphuric acid, gypsum was formed. The new product thus contains considerable calcium.

To observe more exactly the decomposition of the crystals by acids, the following method was used. Some of the hydrated cement containing the crystalline material was separated from the sand grains of the mortar and suspended in a warm dilute solution of gelatin. A drop of this suspension was mounted on a slide with cover glass and cooled till a gel was formed. A drop of the reagent was placed in contact with one edge of the mount while a filter paper was applied to the opposite edge. Thus it was possible to draw the reagent through the preparation slowly enough to make careful microscopic observations. When dilute hydrochloric acid was used, the action progressed slowly from the edges towards the centre of the crystal, leaving an undissolved skeleton form of the original crystal. Experiments with selective dyes (5) and parallel tests with certain silicates and aluminates indicated that the skeleton form of the decomposed crystals consisted mainly of amorphous silica, and that no alumina was present.

Further experiments demonstrated that the crystalline product contained water and lost it only on heating at a high temperature. Thus, heating the hydrated cement containing the crystals at 400° C. for 24 hr. caused a slight apparent roughening of the crystal edges, while prolonged heating at 650° C. rendered the crystals partly isotropic.

These experiments demonstrated that the principal constituents of the new crystalline substance are lime, silica, and combined water, and thus indicated a calcium hydrosilicate. Attempts were therefore made to prepare the crystals from pure materials. A 1 : 10 mixture of pure calcium oxide and quartz sand in a platinum crucible was kept in saturated steam at 150° C. for 48 hr. Microscopic examination of the product showed the presence of a large quantity of the crystals. Crystalline calcium hydroxide was also present, showing that the reaction did not proceed to completion under the conditions of the experiment. However, this method of preparation eliminated all

possibility of the substance containing anything but the oxides of calcium and silicon with combined water. The new calcium hydrosilicate was also obtained by hydrothermal treatment of tricalcium silicate or dicalcium silicate and sand, and also from lime and silica gel (after preliminary hydration and ignition). The product is therefore the result of hydrothermal synthesis under definite conditions, using mixtures of various forms of silica or silicates with lime or with compounds which on hydrolysis yield calcium hydroxide. The synthesis is apparently influenced by temperature, pressure, purity and state of aggregation of the reacting materials and the presence of catalysts such as calcium chloride or sodium chloride. The catalysts appeared to favor the formation of the crystals in certain samples of Portland cement mortar, steam-treated at 150° C.

As this crystalline hydrosilicate is formed on treatment of quartz sand and lime with steam, it may be produced in the process of manufacturing sand-lime bricks. A search of the literature on sand-lime bricks and the hydrothermal formation of silicates gave only meagre information as to the chemical reactions involved or the composition of the products formed. Most workers (2, p. 11; 3, 10) consider that the bonding material is a calcium hydrosilicate of undetermined or variable composition. Some investigators (1, 9) of hydrothermal alteration and synthesis obtained calcium hydrosilicates which they identified as hillebrandite, okenite, and gyrolite. However, the systems usually investigated have been very complex and thus the products have not been homogeneous or readily identified.

While the latter part of the work described in this paper was in progress, reports of extensive researches on the synthesis of hydrosilicates of calcium by Nagai (8) have been published. Mixtures of powdered quartz and calcium oxide in various proportions were treated in saturated steam at temperatures up to 212° C. for 1 to 10 days, and in steam at atmospheric pressure at temperatures up to 1200° C. While mixtures of hydrosilicates were in general formed, preparations were reported composed mainly of: (i) xonotlite ($CaO.SiO_2.\ 0.25H_2O$), (ii) afwillite (of composition $3CaO.2SiO_2.H_2O$ and $3CaO.2SiO_2.8H_2O$) and (iii) hillebrandite ($2CaO.SiO_2.H_2O$).

Preparation of Pure Samples of the Calcium Hydrosilicate

1. *Preparation from Calcium Hydroxide and Quartz Sand*

The quartz sand (20–30 mesh) was treated with dilute potassium hydroxide and then with hot hydrochloric acid. It was finally washed with distilled water till free from chlorides. After all dark or stained grains were discarded, the sand gave, on treatment with hydrofluoric acid, a non-volatile residue of only 0.34%. Calcium oxide, freshly prepared from re-precipitated calcium carbonate by ignition to constant weight at 900° C., was mixed with five times its weight of the prepared sand in platinum crucibles. Water free from carbon dioxide, was added and the samples were stirred to form a thick slurry. The crucibles were placed in an autoclave and exposed to saturated steam at 170° C. for about two weeks. After treatment the samples were dried over

lime and the sand separated by sieving. The fine powder was extracted several times with glycerol-water solution (sp. gr. 1.142) till no free lime could be detected by Emley's method (7) or White's test (15). Filtrations were performed in air, free from carbon dioxide. The water used for washing was also free from carbon dioxide. The extracted material was carefully washed to remove all glycerol, dried over lime to constant weight, and analyzed. The results of the analyses of two preparations are given in Table I.

TABLE I

CHEMICAL ANALYSES OF CALCIUM HYDROSILICATE PREPARED FROM SAND AND CALCIUM OXIDE

	1	2	Calcd. for $2CaO.SiO_2.H_2O$
CaO, %	56.09	57.72	58.95
MgO, %	None	None	
Al_2O_3 and Fe_2O_3, %	0.36	Not weighed	
SiO_2, %	31.83	30.97	31.58
H_2O, %	10.92	10.64	9.47
	99.20	99.33	100.0
Molar ratios			
CaO	1.887	1.997	2
SiO_2	1.000	1.000	1
H_2O	1.144	1.145	1

2. *Preparation from Lime Water and Quartz Crystals and Silica Plates*

Quartz crystals and fused silica plates were suspended in saturated lime water in silver containers, excess lime being placed in the bottom of each container. The samples were treated in an autoclave at 170° C. for periods varying from 7 to 14 days. The crystals and plates were then removed, washed with water, free from carbon dioxide, and dried over lime. Examination showed that the surfaces of the quartz crystals and silica plates were studded with groups of the orthorhombic lath-like crystals. Some of these crystals were 0.15 × 0.5 mm. or more. Fig. 1 shows a photomicrograph of the surface of one of the silica plates.

In obtaining uniform deposits of well defined crystals, different experiments were not equally successful. In some experiments with quartz crystals which had already been treated and the crystalline deposit scraped off, no growth appeared on the quartz, while a deposit of fine needle-shaped crystals was formed on the surface of the mass of calcium hydroxide at the bottom of the container. In other cases, when nickel-plated containers were used to hold the reacting materials, the silica plates were covered with a mixed deposit of the orthorhombic "laths" and fine needles, while large crystals of the former were found attached to the inner surface of the container. In some experiments with silica plates in nickel-plated containers a film of very finely crystalline material of low birefringence, with an occasional orthorhombic "lath" imbedded in the mass, was formed on the surface of the silica plates.

This film flaked off easily leaving the silica plates very clean. After drying this material at 105° C. two analyses, which agreed very well, gave a $CaO : SiO_2 : H_2O$ ratio of 0.86 : 1 : 0.56. The X-ray diffraction pattern of this material differed entirely from those of the "laths" and "needles" mentioned above.

Slight variation in conditions may thus have a large effect on the crystal growth. The temperature of the autoclaves varied considerably at times. This would not only affect the concentration of hydrated lime in solution but might also tend to localize differences in the concentration in different parts of the containing vessel. Koyanagi (6) has demonstrated that a change in the concentration of lime affects, within narrow limits, the crystalline form of hydrated tricalcium aluminate deposited from a solution of alumina cement.

The crystals grown on five large quartz crystals and two silica plates were combined and dried in vacuum over freshly ignited lime. Microscopic examination of the sample showed that it was remarkably uniform and free from amorphous matter. Careful microscopic and chemical tests failed to indicate the presence of either carbonate or hydrate of lime. Fig. 2 shows a photomicrograph of some of the crystals and Fig. 3, the same between crossed nicols. Fig. 4 shows some typical crystals with higher magnification.

A microchemical method of analysis was employed, using a Kuhlmann balance (sensitive to 0.001 mgm.), and samples of 6 to 20 mgm. A procedure avoiding any filtration or transfer of material was used. The water was determined by loss on ignition, the calcium by treating the sample with hydrofluoric acid, weighing the calcium as the fluoride, and the silica by difference. The method was tested out on pure samples of calcium carbonate and dicalcium silicate and found to give good results. The results of three analyses by this method given in Table II indicate definitely a 2 : 1 : 1 compound.

TABLE II

CHEMICAL ANALYSES OF CRYSTALS GROWN ON QUARTZ AND SILICA PLATES

	1	2	3	Calcd. for $2CaO.SiO_2.H_2O$
CaO, %	58.60	58.47	58.45	58.95
SiO_2, %	30.30	30.08	30.36	31.58
H_2O (loss on ignition), %	11.10	11.45	11.19	9.47
Molar ratios				
CaO	2.07	2.08	2.06	2
SiO_2	1.00	1.00	1.00	1
H_2O	1.22	1.27	1.23	1

Physical and Optical Properties of Calcium Hydrosilicate Prepared from Lime Water and Quartz

The optical properties of the orthorhombic crystals found in steam-treated Portland cement mortar have been described by Thorvaldson and Shelton

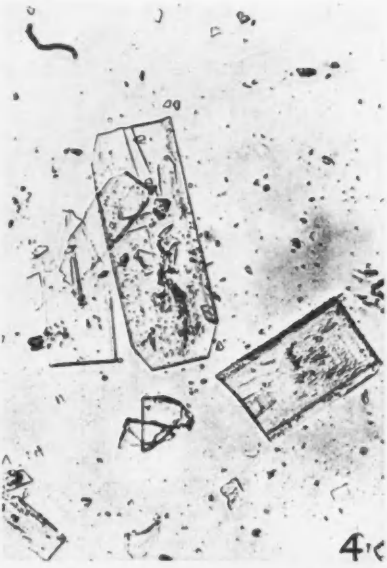

FIG. 1. *Surface of fused silica plate, showing crystals of calcium hydrosilicate. Oblique illumination.* × *22.* FIG. 2. *Crystals of calcium hydrosilicate from silica plates and quartz crystals.* × *88.* FIG. 3. *Same as Fig. 2 with crossed nicols.* FIG. 4. *Typical "lath" crystals from silica plates.* × *220.*

(11). The pure crystals obtained from the quartz and silica plates (analysis given in Table II) gave identical results. The optical data and other characteristics are summarized as follows:—

The crystals are lath-like or prismatic and grow in groups or radiating clusters from the surface of the quartz. Parallel growths and twinning are fairly common. The crystals are colorless and transparent with shining lustre. They are brittle, have a hardness about 5 and specific gravity, as determined with heavy liquids, close to 2.8. They show prismatic cleavage, parallel extinction and positive elongation. The optical character is positive, $Bx_a = Z$. The direction of elongation, parallel to Z, is selected as the crystallographic axis, C. The optic axial plane is parallel to the macropinacoid (100). Consequently only a flash figure is obtained on the ordinarily flat-lying prisms. Rolling a crystal on end gives an acute bisectrix figure. The optic angle thus observed is large and by calculation from the indices of refraction, $2V = 68°$. Indices of refraction are:—

$\alpha_{Na} = 1.614 \pm .002,$
$\beta_{Na} = 1.620 \pm .002,$
$\gamma_{Na} = 1.633 \pm .002$

Birefringence $\beta - \alpha = 0.006$, $\gamma - \alpha = 0.019$

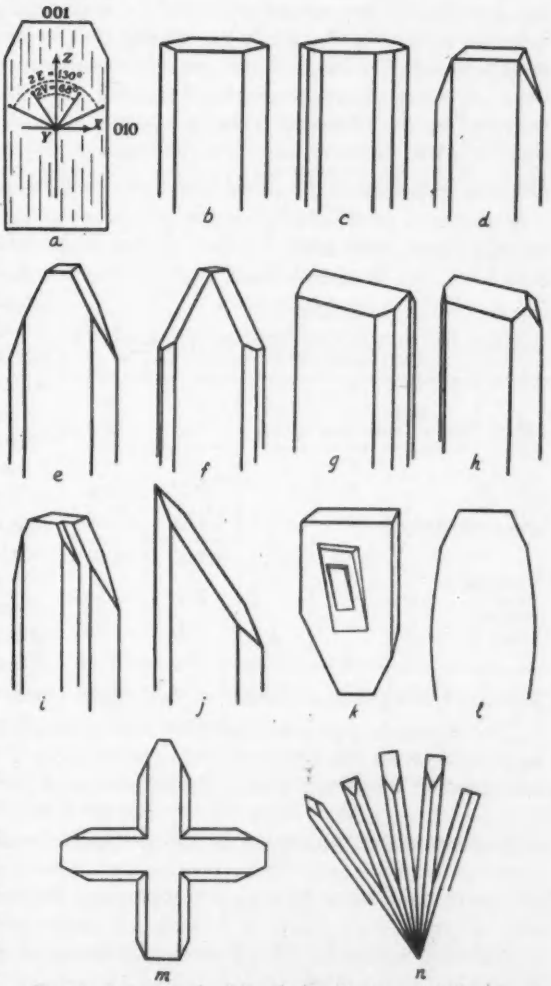

FIG. 5. *Drawings of calcium hydrosilicate crystals from quartz and silica plates. a. Optic orientation and optic angles (2V, 2E) of the illustrated crystals of calcium hydrosilicate. b, c, d, e. Common forms showing basal pinacoids, macropinacoids, prisms, and bracydomes. f. Diagram of form containing pyramids. g and h. Macrodome. i. Parallel growth. j. Hemihedral development. k. Form consisting of pinacoids and bracydomes, with parallel growths on the macropinacoid. l. Barrel-shaped outline of crystals sometimes found in steam-treated cement mortar. m. Cruciform twinning. n. Radial growth.*

Pleochroism and dispersion are not evident. Drawings shown in Fig. 5 *(a)*, *(b)*, *(c)*, *(d)* and *(e)* represent the optic orientation and the forms commonly observed, while *(f)* illustrates the rare occurrence of the pyramid (111) and *(g)* and *(h)* of the macrodome (101). Radiating or parallel growths and twinning occurring frequently are represented by *(n)*, *(i)*, *(k)* and *(m)*. In steam-treated Portland cement mortar curved growth results in the formation of barrel-shaped crystals illustrated in *(l)*. Hemihedral growth is indicated by the rare occurrence of a crystal such as *(j)*. Doubly terminated crystals show, however, that the symmetry is definitely holohedral.

Calcium Hydrosilicate Prepared from Lime and Silica Gel

Mixtures of pure lime and silica gel* in molar ratio of 4 : 1 to give a large excess of lime, were prepared and treated with saturated steam as described above for the lime and sand preparation, except that there were several treatments with intermediate grinding of the samples. The preparations were extracted with a glycerol solution to remove the excess of free lime, washed and dried at 105° C. to constant weight. The product was fairly homogeneous, and consisted of fine needle crystals instead of the lath-like plates described above. The material differed also in optical properties and X-ray diffraction pattern. Results of analysis in duplicate of two preparations are given in Table III.

TABLE III

ANALYSIS OF CALCIUM HYDROSILICATE OCCURRING AS NEEDLE-SHAPED CRYSTALS

Sample Total time in autoclave (days)	1 32	2 26
CaO, %	58.27	57.57
SiO_2, %	29.30	28.52
Loss on ignition, %	11.76	12.86
	99.33	98.95
Molar ratios		
CaO	2.13	2.16
SiO_2	1.00	1.00
H_2O	1.34	1.50

The extremely fine subdivision of the material no doubt favored the adsorption of both calcium hydroxide and of water. Further, the exposure to air during grinding and during the extraction of the excess of free lime gave, in spite of precautions, opportunity for the formation of some calcium carbonate through the absorption of carbon dioxide by the free calcium hydroxide. These samples were therefore not as pure as those obtained by growing crystals on quartz and silica plates. The analyses, however, indicate a compound with a lime-silica ratio of 2 : 1 with one mole or possibly more of water. Slightly high values for calcium oxide and for loss on ignition are to be expected.

Optical Properties of Needle Crystals from Lime and Silica Gel

The crystals occurred usually in radiating clusters or masses and also detached. They are anisotropic, very weakly birefringent, with positive elongation and parallel extinction. With the oil immersion they are found to be thin prisms usually having needle-like or incomplete terminations. Some twinning and parallel growths were observed. No interference figures

**The silica gel passed through a 300-mesh sieve and contained 87.1% SiO_2. Loss on ignition was 12.5%, and non-volatile residue with hydrofluoric acid, 0.4%.*

were obtainable so the optical character was not determined. The mean index of refraction was found to be $1.597 \pm .003$. The refractive index is thus decidedly lower than the indices for hillebrandite, but close to those of foshagite. The other optical properties, as far as they were determined, are similar to those of the natural minerals. The X-ray diffraction pattern (Table IV and Fig. 6), however, indicates that these crystals represent another distinct form of hydrated dicalcium silicate.

TABLE IV

X-RAY DATA

Material obtained from steam treated Portland cement mortar		Calcium hydrosilicate crystals prepared from saturated lime water and quartz crystals		Calcium hydrosilicate crystals prepared from excess lime and silica gel		Hillebrandite. Sample from Velardena Mine, Durango, Mexico, according to Vigfusson (14)		Calcium hydroxide according to Harrington (4)	
Planar spacing d_{hkl} in Å	Estimated relative intensity	Planar spacing d_{hkl} in Å	Estimated relative intensity	Planar spacing d_{hkl} in Å	Estimated relative intensity	Planar spacing d_{hkl} in Å	Estimated relative intensity	Planar spacing d_{hkl} in Å	Estimated relative intensity
3.51	W	3.53	W	3.50	W	3.51	W		
3.27	SS	3.28	SS	3.32	WWd	3.34	M		
						3.13	W	3.11	M
3.08	M	3.08	WW	3.05	W				
				2.93	SS	2.93	SS		
2.87	Md	2.88	M						
2.80	Md	2.82	M	2.77	W	2.79	M		
2.72	Md	2.68	M	2.67	M	2.68	W		
2.60	Md	2.60	M					2.63	SS
2.52	Md	2.53	W			2.46	M		
2.42	S	2.42	S	2.38	M	2.38	WW		
2.30	Md	2.32	M			2.30	M		
2.25	Md	2.24	M	2.26	S	2.22	W		
2.17	WW	2.16	W			2.16	M		
2.07	Sd	2.07	S	2.07	W	2.10	W		
2.00	Md					2.04	M		
1.987	Md	1.957	M	1.958	S	1.960	M		
1.927	Md	1.925	M	1.872	S	1.875	W	1.930	S
		1.845	W	1.810	S	1.820	S		
1.785	S	1.786	S	1.763	W			1.795	S
1.717	M	1.724	Wd	1.714	WW	1.737	S		
						1.675	WW	1.685	M
1.647	S	1.650	S	1.633	Wd	1.623	WW		
1.563	Md	1.566	M			1.595	M		
				1.548	Wd	1.560	WW	1.555	W
1.535	Md	1.534	M			1.528	M		
				1.518	Wd	1.507	W		
1.475	Wd	1.475	W	1.469	WW	1.467	W	1.480	M
1.446	Wd	1.443	W			1.442	W	1.450	M
				1.415	WW	1.432	W		
1.400	Wd	1.400	W	1.363	W				
1.352	Wd	1.355	M	1.333	WW	1.350	W		
1.305	WW	1.308	W			1.301	W	1.312	M
				1.284	WW	1.262	M		
1.250	Wd	1.246	W						
1.230	Wd	1.228	W	1.223	WW	1.210	W		
				1.178	S	1.183	M	1.175	WW
1.156	Md	1.160	M	1.152	WW	1.149	M	1.144	M
1.138	Md	1.138	M						
				1.122	W	1.121	M	1.128	W
1.112	WW	1.110	W						
1.090	WW	1.088	WW	1.090	Wd				
				1.059	WWd	1.060	M	1.061	M
1.038	WW	1.040	WW	1.032	WW	1.038	M	1.038	W
1.010	WW	1.008	WW					0.013	W

Estimated relative intensity: SS = very strong; S = strong; M = medium; W = weak; WW = very weak; d = diffuse.

X-ray Data

The products were studied by the powder method. Photographs of the X-ray diffraction patterns were made with a General Electric Company multiple spectrograph. A Coolidge tube with molybdenum target was the source of the X-rays and a zirconia filter was used in front of the film. Table IV gives the planar spacings and estimated relative intensity of the diffraction lines. Pure sodium chloride was used as a standard to correct the planar spacings. For comparison, patterns for hillebrandite (14) and for calcium hydroxide (4) are included in the table. The data in Table IV were charted in Fig. 6 for ready comparison, the height of the lines corresponding to the relative intensity of the diffracted X-ray beam. Examination of the data shows that the pattern for the orthorhombic crystals agrees well with the pattern obtained with material from steam-treated mortar, but is entirely different from the patterns given by calcium hydroxide (4), hillebrandite and foshagite (14), or other known calcium hydrosilicates. The pattern for the "needle" crystals shows a slight similarity to the one for hillebrandite but is in general different.

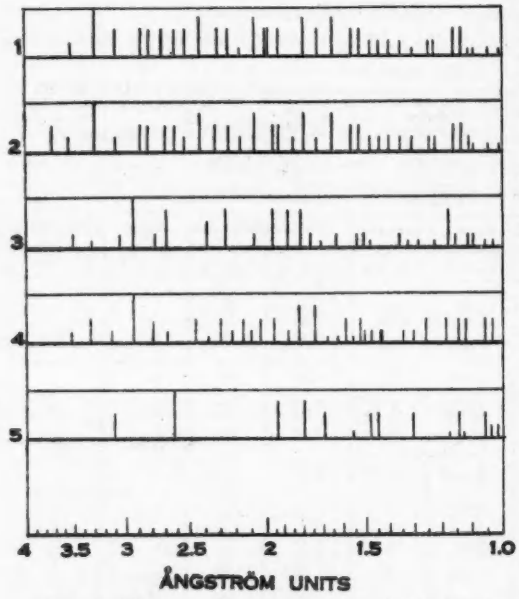

FIG. 6. *Diagrammatic representation of X-ray patterns of the following substances. 1. Material obtained from steam-treated Portland cement mortar. 2. Calcium hydrosilicate crystals ("laths") from quartz and silica plates. 3. Calcium hydrosilicate crystals ("needles") from silica gel and excess lime. 4. Hillebrandite from Velardena Mine, Durango, Mexico. 5. Calcium hydroxide.*

Acknowledgments

The X-ray photographs were made at the Department of Geology and Geography, University of Wisconsin, through the courtesy of Dr. A. N. Winchell. The authors are indebted to Mr. A. L. C. Atkinson for making the drawings.

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VAPOR DENSITY OF SULPHUR DIOXIDE[1]

By W. W. Stewart[2] and O. Maass[3]

Abstract

The technique developed in this laboratory for measuring gas densities has been made still more sensitive by using a 50-litre volume. The experimental results obtained showed that the apparent molecular weight-pressure isothermal for sulphur dioxide is not a straight line. This is in agreement with the equation of state for gases at low pressures, the study of which has been the main object of this investigation. From the data on sulphur dioxide its true molecular weight was found to be 64.075.

Introduction

The density of sulphur dioxide has been measured at 25° C. and at and below atmospheric pressure and at 0° C. and atmospheric pressure by a method developed in this laboratory. The measurements are correct to within 0.01%. The details of the experimental arrangement have been discussed by Cooper and Maass (2). In the present communication a modification of their apparatus, the introduction of a 50-litre constant volume, will be discussed, as well as corrections which have been applied to the measurements of pressure and mass.

The following units have been used in the calculations and the standardization. With the exception of the value for the density of water these constants are those given by Birge (1): $g_{45}=980.616$, 1 litre $=1000.027$ cm^3., ice point $=273.18°$ A., $d(H_2O)$ at 24.90° C. $=0.9970995$ gm./ml., $R=0.082051$ litre atm./moles °A.

Experimental Work

The largest constant volume used in this method by previous workers was five litres. In the present work the constant volume has been increased to about 50 litres, which has increased the precision of the measurement of the mass of the gas and also reduced the adsorption correction. This volume has been calibrated to within 1 part in 100,000.

The constant volume was constructed from a well aged Pyrex balloon flask. The neck was drawn down to a 1 cm. tube and after completing the calibration a 1 cm. bore stop cock was sealed to this tube.

After carefully cleaning and drying the inside of the constant volume it was mounted in a 45 gallon oak cask which served as a constant temperature bath. The water in the bath was well stirred and the temperature of the bath could be controlled to within 0.002° at 25° C.

It is quite evident that the usual method of calibrating volumes by direct weighings is not feasible for such a large volume. The method adopted for the calibration is independent of the gas laws and depends upon filling the flask up to a definite mark with a known weight of air-free distilled water. The experimental arrangement for filling the constant volume is shown in Fig. 1

[1] *Manuscript received July 14, 1934.*
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The weight pipette had a capacity of about 5000 gm. A ground glass cap fitted the end of the delivery tube and the stop cock was closed during the weighings. The pipette was filled with air-free distilled water. It was placed in the balance case for half an hour and then weighed on both pans of the balance. The mean of these two weights was taken as the weight of the full pipette. As the water syphoned into the constant volume it was replaced by dry air free from carbon dioxide. The empty pipette was weighed in a manner similar to that described above. This procedure was continued until the constant volume was almost filled. The final addition of water was made from a 100 gm. weight pipette.

During the additions of water to the constant volume the temperature of the constant temperature bath was held at 24.90° C. It was assumed that the temperature of the water in the constant volume was at the temperature of the bath when the position of the meniscus of the water in the neck of the flask remained in a steady state. The position of the meniscus was observed with a reading telescope and was recorded in reference to graduations etched on the neck of the volume. This position was used as the reference mark in further calibrations.

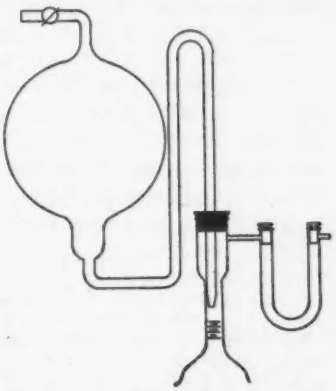

FIG. 1. *Calibration weight pipette.*

The U-tube shown in the diagram was filled with "Dessichlora". It was weighed before and after the addition of water to the constant volume. From these observations the weight of water lost by evaporation was calculated.

The constant volume was calibrated up to the reference mark by two independent determinations. Then the stop cock was sealed to the neck of the balloon and the volume of the neck above the reference mark up to the top of the stop cock was determined by adding a weighed amount of water from a small pipette.

The large weight pipette was weighed on a 10 kgm. balance. The sensitivity of balance under a 5000 gm. load was 0.010 gm. per 0.5 scale divisions. The weights were compared against a standard set of weights directly up to 50 gm. and then by intercomparison in the usual manner. During each weighing the barometric pressure, temperature and humidity of the balance room were observed, so that each individual weight could be reduced to the vacuum standard.

The results of the two determinations of the volume at 24.90° C. are given in Table I.

The volume of the constant volume at 24.90° C. used in the calculations as V was 48.3184 ± 0.0004 litres.

TABLE I

CALIBRATION DATA FOR THE CONSTANT VOLUME

—	1	2
Weight of water added to flask (*in vacuo*), gm.	48160.67	48161.64
Weight of water lost by evaporation, gm.	0.13	0.36
Net weight of water in flask, gm.	48160.54	48161.27
Volume of flask to the reference mark, ml.	48300.64	48301.37
Mean volume of flask to the reference mark, ml.	48301.00 ± 0.37	
Volume of the neck and the stop cock, ml.	17.37	17.41
Mean volume of the neck and stop cock, ml.	17.39 ± 0.02	
Total mean volume of the flask at 24.90° C., ml.	48318.39 ± 0.39	

It is necessary to apply two corrections to this value to obtain the correct volume corresponding to the temperature and pressure of any individual set of observations. The first is a correction for the temperature coefficient of the Pyrex balloon. This has been calculated from the equation given by Keyes (6). The second is a correction for the contraction of the volume due to a difference in pressure on the constant volume when the gas is at a pressure below atmospheric. This correction was determined by experiment using the method of Rayleigh. The results shown in Table II were obtained for the contraction in volume at various differential pressures. These measurements show that the decrease of the volume of the balloon is a linear function of the differential pressure, which agrees with the results of Moles and Mirvalles (8).

TABLE II

THE CONTRACTION IN VOLUME AT VARIOUS DIFFERENTIAL PRESSURES

P, cm.	75	50	25	10
V, ml.	7.37	4.91	2.44	0.97

The measurement of the pressure of the gas and the corrections applied to reduce the observed pressure to 0° C. 45° Lat. and sea level have been described by Cooper and Maass (3). In the present work an additional correction to the observed pressure has been introduced. The pressure required in the calculation is the mean pressure in the constant volume, that is, the pressure on a horizontal plane passing through the centre of the volume. Therefore, the mercury meniscus on the gas side of the manometer should lie in this plane. In the actual experimental arrangement this meniscus was about 38 cm. above the horizontal plane, so the actual pressure registered on the manometer was less than the pressure at the centre of the volume by an amount which is due to the variation of the pressure with height.

This correction was calculated for each pressure measurement from the equation

$$\log. p_c/p = MH/RT \times 1000 \times 1033.3,$$

where p_c is the pressure at the centre of the balloon and p the observed pressure; H is the difference in height in cm. between the mensicus and the centre of the balloon. M, the molecular weight of the gas, was calculated

from the ideal gas laws using the uncorrected pressure. At 25° C. and 250 mm. pressure, the correction amounts to 0.054 mm. and at 750 mm. pressure it is 0.145 mm. The error in the correction due to the method of calculation was less than 1% in every observation.

The weight of the gas is obtained by condensing the gas from the constant volume into small weighing tubes which are sealed off and weighed at room temperature. The tubes were shaped similarly to those used by Cooper and Maass (2). They were blown from 2 mm. wall Pyrex tubing. The capillary stem was of about 1 mm. bore and 2 mm. wall. These tubes were strong enough to stand the pressure of the condensed gas at room temperature and no special precautions were taken in handling them. The size of the tubes depended upon the weight of the gas condensed from the constant volume. The volumes of the tubes were about 60, 100, and 175 cc.

The technique of condensing the gas into the tubes was somewhat different from that of previous workers. After carefully cleaning the surface of the tubes, the first stage of the condensation was done by using solid carbon dioxide-ether mixture until the pressure of the gas was reduced to about 2 cm.; then the remaining portion of the gas was condensed into the tube by using liquid air as the refrigerant. If only liquid air was used, the condensation was very slow as the tubes filled with fine needles of solid sulphur dioxide.

After sealing off the tubes they were placed in a cabinet conditioned with dry air until they were in equilibrium with room temperature. The tubes were left in the conditioning cabinet for at least 12 hr. before being weighed directly on the balance pans.

Since in all cases the weight of the gas was of the order of 40 gm., the weighing of these tubes presented no serious difficulties, and could be made with a high degree of precision by observing the usual precautions necessary in handling a chemical balance.

The observed weight of gas was reduced to vacuum standard in each case as outlined by Cooper and Maass (2). An additional correction to the weight of the gas has been introduced, that is, the correction for the amount of gas adsorbed on the surface of the constant volume at the initial pressure. If this factor is neglected the calculated apparent molecular weight is too large, as this adsorbed gas did not contribute to the initial pressure but was condensed out when the pressure was reduced to almost zero pressure. Therefore the amount of gas adsorbed on the surface of the volume has to be subtracted from the observed weight of gas to obtain the true apparent molecular weight. Moles (7) has pointed out that this correction for adsorption has to be considered in all physico-chemical methods for determining molecular weights of gases, and recommends that the size of the volumes be about 1000 cc., as the adsorption correction is reduced by increasing the radius of the balloon. This is about the limit of the volume that can be conveniently handled in the "classical balloon method". By using a constant volume of approximately 50 litres the adsorption correction has been reduced almost to the precision required for the measurement of mass of the gas.

The amount of sulphur dioxide adsorbed on the surface of the constant volume at various pressures has been calculated from the data of Crespi and Moles (5). The data in Table III are those used in the adsorption correction at 25° C.

TABLE III

INFLUENCE OF PRESSURE ON AMOUNT OF SULPHUR DIOXIDE ADSORBED ON THE GLASS SURFACE

P, atm.	1	1/2	1/3	1/4	1/5	1/6	1/7	1/8
SO_2 adsorbed, gm. $\times 10^4$	53.0	37.6	30.6	25.6	23.7	21.8	20.0	18.7

The temperature of the gas is required to within 0.01° C. in order to retain the precision desired in the calculation of M'. The temperature observed at 25.00° C. and at the ice point were well within this limit. At 25° C. the bath was maintained to within 0.002° C. during the run. The temperature of the bath was read on a mercury standard thermometer, PTR 3191, graduated in 0.1° C. In the runs at 0° C. the bath was filled with snow and water. The circulation of the bath liquid was vigorous, and no variation of temperature could be detected by placing a Beckmann thermometer at various positions in the bath. The temperature of the bath remained constant to within 0.002° C. The temperature was determined by a Beckmann thermometer which had been calibrated in a freezing point apparatus, using freshly distilled water, immediately before and after a run.

The sulphur dioxide was obtained from a tank of c.p. material. The gas was purified by fractional distillation under vacuum in an air-free apparatus as described by Cooper and Maass (3).

Experimental Results

The experimental results are shown in Table IV, and graphically in Fig. 2. The last column of the table records the values of the apparent molecular weight for the temperatures and pressures shown in Columns 1 and 3. In the fifth column, w is the weight of the gas corrected for adsorption. The graph shows the mean value of the apparent molecular weight as a function of the pressure. The isothermals are seen to possess a slight curvature, which is contrary to what is expected from the results of other workers. Previously the isothermals for sulphur dioxide were found to be straight lines to within the experimental error.

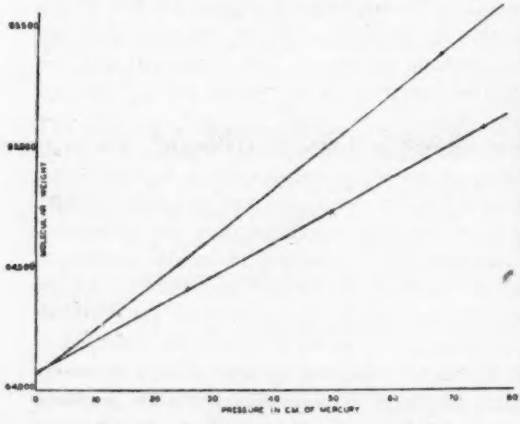

FIG. 2. *Isothermals of sulphur dioxide.*

TABLE IV

ISOTHERMALS AT 25 AND 0° C.

Pressure, mm. Hg.	Residual press., mm.	Temp., °A	V, litres	w, gm.	M', mol. wt.
A. Isothermal at 25° C.					
749.330	0.700	298.18	48.3184	126.646	65.1006
742.449	0.540	298.18	—	125.497	65.0892
753.762	0.787	298.18	—	127.390	65.1049
Mean pressure, 748.514 mm.; mean mol. wt., 65.0982; deviation of mean, 0.0007%.					
482.614	1.207	298.18	48.3156	80.9661	64.7208
493.010	0.270	298.18	48.3157	82.5420	64.7441
498.678	0.820	298.18	48.3151	83.7563	64.7440
505.266	0.300	298.18	48.3158	84.9596	64.7492
Mean pressure, 494.892; mean mol. wt., 64.7395; deviation of mean, 0.0028%.					
253.026	0.255	298.18	48.3135	42.3112	64.4218
258.988	0.508	298.18	—	43.2677	64.4216
258.411	0.519	298.18	—	43.1762	64.4187
256.653	0.700	298.18	—	42.9533	64.4267
258.734	1.146	298.18	—	43.1210	64.4261
256.364	1.570	298.18	—	43.6601	64.4334
252.701	3.354	298.18	—	41.7382	64.4194
Mean pressure, 256.411 mm.; mean mol. wt., 64.4239; deviation of mean, 0.0025%.					
B. Isothermal at 0° C.					
705.694	0.415	273.15	48.3059	130.894	65.4411
649.590	0.425	273.15	48.3055	120.316	65.3532

The calculation of M' has been based on the equation $M' = wRT/PV$. A typical calculation is given in Table V. This shows the results of a complete experiment together with all the corrections necessary in the calculations.

TABLE V

EXAMPLE OF EXPERIMENTAL DATA AND CALCULATION OF M'

Temperature of constant volume, ° C.		25.0	
Temperature of cathetometer scale, ° C.		24.9	
Temperature of manometer bath, ° C.		28.48	
Initial pressure, mm. of Hg.	254.15	245.16	254.155
Residual pressure	0.26	0.25	0.255
Volume of dead space, litres		0.150	
Volume of constant volume at 25.00° C. and $P = 50$ cm., litres		48.3135	
Weight of tube and gas, gm.		106.7848	
Weight of tube and air, gm.		64.5510	
Weight of gas uncorrected, gm.		42.2338	
Weight of tube and distilled water, gm.		137.297	
Volume of tube, cc.		7.95	
Weight of air in tube, gm.		0.0863	
Weight of air displaced by weights, gm.		0.0059	
True weight of gas *in vacuo*, gm.		42.3142	
Wt. of gas adsorbed at 25 cm. on the surface of volume flask, gm.		0.0030	
Temperature correction to pressure, mm.		−1.192	
Level correction to pressure, mm.		0.054	
Gravity correction to pressure, mm.		0.009	
Pressure corrected to 0° C. 45° Lat. and sea level, mm.		253.026	
Corrected residual pressure, mm.		0.254	
Weight of gas corrected for adsorption, gm.		42.3112	
Apparent molecular weight, M'		64.4218	

M' has been calculated in all cases from Equation (1), which is based on the following.

The weight of gas in the constant volume V under a pressure p and a temperature T is $W=PVM'/RT$, where M' is the apparent molecular weight of the gas.

Similarly, the weight of the gas in the constant volume V at a temperature T and residual pressure p is $w=pV'M''/RT$, and the weight of gas in the dead space v at the residual pressure p and temperature t is $w''=pvM''/Rt$.

If the weight of the gas adsorbed at a pressure P is w''' and the weight of the gas condensed from the volume, corrected to *vacuo*, is W', then $W=W'+w+w''-W'''$. Therefore

$$M' = \frac{RT(W'-w''')}{PV} + \frac{pV'M''}{PV} + \frac{pvM''T}{PVt} \qquad (1)$$

The value of M'', the apparent molecular weight of the gas at the small residual pressure p, is very nearly that of the true molecular weight of the gas. In all calculations M'' is taken as 64.06.

V' is the volume of the constant volume corrected for a differential pressure of 75 cm. The value of V' used is 48.311 litres.

For the experimental data given above

$$M' = 64.3571 + 0.0645 + 0.0002 = 64.4218 .$$

Discussion

The maximum error in the apparent molecular weight estimated from deviations assigned to the four measurements, pressure, temperature, weight and volume, varied at 25° C. and 0° from 0.014% at the highest pressure to 0.027% at the lowest pressure. An examination of the data in Table IV (*A*) will show that these are maximum deviations between any single value of the molecular weight and the mean value, if the values be compared at the same temperatures and pressures.

The average deviation of the mean of the molecular weight is shown in the table. The value of the molecular weight at any point near the mean was corrected to its value at the mean pressure, then the average deviation calculated in the usual manner. These data indicate that the mean values of the molecular weight are correct to less than 0.01%.

The three values obtained for the 25° C. pressure isothermal do not lie on a straight line. A straight line drawn through any two points will miss the third by an amount many times the experimental error. This result is not unexpected. The equation which has been developed in connection with this work (4) namely,

$$\frac{M'}{M_o} = 1 + \left(\frac{a - \frac{RTb_o}{1+KT}}{R^2T^2}\right)P + 2\left(\frac{a - \frac{RTb_o}{1+KT}}{R^2T^2}\right)^2 P^2 + \ldots\ldots\ldots \qquad (2)$$

can conveniently be written as

$$\frac{M'}{M_o} = 1 + SP + 2S^2P^2 + \ldots\ldots\ldots$$

For carbon dioxide the valves of a, b_o and K are such that S^2 becomes insignificant for pressures of an atmosphere and less. With sulphur dioxide this is not the case. Taking Cooper and Maass' (3) data on sulphur dioxide, it can be shown that the value for S is such that the third term is significant.

The general equation of the isothermal is

$$M' = M_o + bP + CP^2 \tag{3}$$

or

$$\frac{M'}{M_o} = 1 + \frac{bP}{M_o} + \frac{CP^2}{M_o} \tag{4}$$

From Equations (2) and (4), $C = \frac{2b^2}{M_o}$, so the equation for the isothermal is

$$M' = M_o + bP + \frac{2b^2}{M_o} P^2 \tag{5}$$

The values for M_o and b which fit the experimental data most accurately were determined in the following way. From the graph a tentative value for M_o was obtained and the value of the mean molecular weight at the highest pressure was assumed to be correct. From these two values, b was calculated from Equation (5). Then M' was calculated, using the above constants in Equation (5), for the other observed pressures. From an examination of the deviation between the observed molecular weights and the calculated ones, the constants M_o and b could be varied to give an equation that represented the experimental data more accurately. Table VI shows the results calculated from three sets of constants and the deviation between the calculated and observed data.

TABLE VI

CALCULATION OF THE EQUATION OF THE ISOTHERMALS

P, mm.	M' obs.	M' calc.	Deviation	
$M' = 64.0800 + 1.0029\,P + 0.03130\,P^2$				
256.411	64.4239	64.4219	+0.0020	0.0031%
494.892	64.7395	64.7461	−0.0066	0.0010%
748.514	(65.0982)	65.0982	+0.0000	
$M' = 64.0750 + 1.0075\,P + 0.03168\,P^2$				
256.411	64.4239	64.4185	0.0054	0.0084%
494.892	64.7395	64.7446	−0.0051	0.0079%
748.514	(65.0982)	(65.0982)		
$M' = 64.0650 + 1.0170\,P + 0.03229\,P^2$				
256.411	64.4239	64.4152	0.0087	0.013%
494.892	64.7395	64.7429	−0.0034	0.005%
748.514	(65.0982)	(65.0982)		

The equation $M' = 64.0750 + 1.0075\,P + 0.03168\,P^2$ represents the observed data to within the maximum error of each mean molecular weight. It represents the data better than the other two equations do. The value M' 65.0982 at $P = 74.8$ cm. was assumed to be correct for purposes of calculation. This value may have a maximum error of ± 0.0008 as shown in Table IV (*A*). If M' (65.0982) is varied by -0.0008 the variation in the calculated M_o(64.0750) is ± 0.0006; and b(1.0075) varies by ± 0.0005. Therefore, the isothermal of the molecular weights of sulphur dioxide at 25° C. can be represented in the equation

$$M' = 64.075 + 1.0075\,P + 0.03168\,P^2.$$

The equation for the zero degree isothermal is found to be

$$M' = 64.0750 + 1.4262\,P + 0.06344\,P^2,$$

by putting $M_o = 64.0750$, as obtained from the 25° C. isothermal and calculating the numerical constants from the zero degree data in the same way as in the case of the 25° C. isothermal.

A comparison with the data of Cooper and Maass (3) is made by using the equations obtained for the isotherms and calculating the value of M' for pressures corresponding to their data. In making their calculations they omitted to consider the adsorption correction already described. Furthermore, they used for R the value 0.082046, which is the value for the normal atmosphere, while their pressures were expressed in terms of the atmosphere at 45° Lat. Consequently, their results have been recalculated making a correction for adsorption and using the correct value of R corresponding to the atmosphere at 45° Lat. These recalculated values are used for the purpose of a comparison with the results obtained in the present work. The figures are shown in Table VII.

TABLE VII

COMPARISON OF DENSITY DATA

T, ° A.	P, cm. Hg.	Cooper and Maass	Present work	Difference
273.18	71.496	65.475	65.473	+.002
	43.560	64.905	64.896	+.009
	24.074	64.552	64.533	−.019
298.18	68.856	65.023	64.013	+.010
	45.956	64.697	64.698	−.001
	23.659	64.410	64.391	+.009

It is seen that the agreement in all cases is within the limits of experimental error. This indicates that Cooper and Maass' assumption that the isotherm is a straight line was erroneous. Actually the data conform much better to the equation for a curved isotherm obtained in the present work.

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THE EVOLUTION OF CARBON DIOXIDE IN THE A.-C. ELECTROLYSIS OF SODIUM CARBONATE AND BICARBONATE SOLUTIONS, AND THE DISCHARGE POTENTIALS OF CARBONATE AND BICARBONATE IONS[1]

By J. W. Shipley[2]

Abstract

The a.-c. electrolysis of sodium carbonate solutions at voltages as high as 110, even when arcing occurs on the electrodes, does not cause the evolution of carbon dioxide. In the a.-c. electrolysis of aqueous bicarbonate solutions with platinum electrodes, hydrogen, oxygen and carbon dioxide are evolved freely until all the bicarbonate has been transformed to carbonate, after which the evolution of carbon dioxide ceases and only hydrogen and oxygen are given off. In a.-c. electrolysis of sodium bicarbonate solutions and solutions of the sodium salts of aliphatic acids, a deposit of finely divided platinum is formed on the electrodes. This deposit inhibits the evolution of carbon dioxide, hydrogen and oxygen, but does not affect the current flow. The decomposition potential of bicarbonate solutions in respect to the evolution of carbon dioxide on smooth platinum and with d.c. was found to be 2.2 volts, and of carbonate solutions, 3.5 volts. The anodic discharge potential of HCO_3^- is -1.45 to -1.50 volts, and of CO_3^{--}, -1.90 to -1.95 volts. The evolution of carbon dioxide does not appear to cause any polarizing effect on the anode.

Experimental

During the a.-c. electrolysis of aqueous solutions of the sodium salts of aliphatic acids, using platinum electrodes, carbon dioxide was found to be one of the components of the gaseous products of electrolysis. An examination of the residual solutions disclosed the presence of carbonates and bicarbonates in solution. These had been formed from the sodium organic salt during electrolysis. Before proceeding further it was decided to observe the behavior of pure sodium carbonate and bicarbonate solutions electrolyzed at 110 volts and 60 cycles a.c.

A.-C. Electrolysis of Sodium Carbonate and Sodium Bicarbonate Solutions

Carbon dioxide was not evolved when solutions of various concentrations of freshly fused sodium carbonate in water free from carbon dioxide were electrolyzed at 110 volts a.c. and currents as high as 7.2 amp. per sq. cm. on platinum electrodes. Hydrogen and oxygen were evolved freely as in the a.-c. electrolysis of water (5) containing sodium hydroxide. Even when the temperature was allowed to approach the boiling point of the solution and with arcing occurring on the electrodes no evolution of carbon dioxide could be detected.

Carbon dioxide was evolved copiously from a sodium bicarbonate solution, electrolyzed under similar conditions, at all dilutions and at temperatures as low as 18° C., at 2.5 volts. At low current densities (0.5 amp. per sq. cm.) the evolution of carbon dioxide was small.

[1] *Original manuscript received July 29, 1934.*
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As electrolysis proceeded the electrodes became covered with a finely divided, loosely adhering coating assumed to be platinum black. As this deposit grew, the evolution of gases diminished and finally ceased, without affecting the flow of current. Even at high current densities this phenomenon was observed unless arcing on the electrodes resulted in the loosening of the deposit and its removal from the electrode surface. When this occurred, evolution of gas recommenced and continued until a new deposit was built up. Apparently the products of electrolysis recombined on the surface of the electrodes.

When the evolved gases (hydrogen, oxygen and carbon dioxide), collecting in the electrode chamber above the electrolyte, were left standing for a few hours, they recombined completely, sometimes with a slight explosion. The reaction is attributed to the catalytic effect of the finely divided platinum adhering to the upper walls of the electrode chamber, with which the gases were in contact.

Continued a.-c. electrolysis of sodium bicarbonate solution resulted in a mixture of carbonate and bicarbonate, the proportions depending on the rate of evolution of carbon dioxide, and on the temperature. Complete conversion of the bicarbonate to carbonate took place in less than three hours at 45° C. at 110 volts and 60 cycles a.c. Of course, at the boiling point the evolution of carbon dioxide due to the partial pressure of this gas would eventually result in the transformation of bicarbonate to carbonate, even in the absence of electrolysis, but continuous boiling of a portion of the bicarbonate solution used in this electrolysis did not free the solution from bicarbonate after six hours' boiling.

The composition of the gas evolved at 110 volts a.c. and 3 amp. per sq. cm. using bright platinum electrodes was: carbon dioxide, 33.3; oxygen, 23.3; hydrogen, 42.0%. The electrolyte was a 2 *N* solution of sodium bicarbonate kept at 18° C. The proportions of carbon dioxide, hydrogen and oxygen in the evolved gases remained practically the same when the current density was raised to 7 amp. per sq. cm., and arcing occurred on the electrodes, but as the amount of platinum black formed on the surface of the electrodes increased, the evolution of carbon dioxide decreased and finally fell to zero, and hydrogen and oxygen only were evolved in diminishing quantities until their evolution finally ceased. The current, however, remained constant even after all evolution of gas had ceased.

In the electrolysis of bicarbonate solutions with iron electrodes the gases were produced at first in the same proportions as when bright platinum electrodes were used, but although the production of carbon dioxide gradually diminished and ceased, hydrogen and oxygen continued to be evolved. The electrodes corroded rapidly with the production of the hydrated oxides of iron.

Decomposition Potential of Carbonate and Bicarbonate Solutions in Respect to the Evolution of Carbon Dioxide

A search of the literature available disclosed nothing definite in regard to the potential at which carbon dioxide is evolved from bicarbonate and

carbonate solutions at a platinum electrode. Experiments were carried out to determine the decomposition potential at which carbon dioxide was freed from these ions in d.-c. electrolysis. The presence of carbon dioxide in the evolved gas was detected by passing the anodic gas into barium hydroxide solution. The low partial pressure of carbon dioxide in the solutions used did not interfere with the determination, since the amount of carbon dioxide carried over by the evolved oxygen below the discharge potential of the HCO_3^- was so small as not to interfere with the detection of the carbon dioxide liberated when the discharge potential of the HCO_3^- was reached.

The electrolysis was carried out in a small beaker exposed to the air. The bright platinum electrodes were 12 × 6 mm., and over the anode was a glass tube, immersed to the base of the electrode, from which the evolved anodic gases passed into a capillary tube in the barium hydroxide solution. A plug of cotton wool intercepted the spray that might come over from the anolyte. The barium hydroxide solution was protected from the air by a plug of cotton wool kept moist with sodium hydroxide solution.

A preliminary experiment with sodium hydroxide solution showed that hydrogen and oxygen were freely evolved in the above apparatus at a voltage of 1.9, so it was assumed that from a carbonate or bicarbonate solution any carbon dioxide evolved and not reabsorbed would be carried over with the oxygen from the anode and absorbed by the barium hydroxide solution, forming barium carbonate.

Decomposition Potential of Sodium Carbonate Solutions

Tenth-normal sodium carbonate solution was prepared from freshly fused sodium carbonate dissolved in carbon dioxide-free water. The first indication of carbon dioxide evolution on electrolysis was observed at 3.5 volts with a current density of 0.01 amp. per sq. cm. and at 20° C. At 4.0 volts the evolution of carbon dioxide was rapid. When a little sodium hydroxide solution was added to the electrolyte the voltage necessary to cause evolution of carbon dioxide appeared to be somewhat greater, and when a considerable amount of sodium hydroxide was added the evolution of carbon dioxide was completely inhibited even at voltages up to 110 d.c. and temperatures approaching the boiling point. With the rapid evolution of oxygen under these conditions, and with the top of the anode above the surface of the electrolyte, it was thought that not all of the carbon dioxide would be reabsorbed by the electrolyte.

The above determinations were repeated using various concentrations of sodium carbonate but with the same results. More concentrated solutions gave the same decomposition potential as the more dilute, and the evolution of carbon dioxide was inhibited by the addition of sodium hydroxide even when the voltage was raised to 110 d.c., and the electrodes became hot and arcing occurred.

The addition of sodium sulphate to the carbonate solution even up to the saturation point did not inhibit the evolution of carbon dioxide, so the

explanation of the effect of sodium hydroxide does not lie in the depression of the CO_3^{--} concentration by the excess Na^+ provided by the sodium hydroxide.

Potassium carbonate solutions were prepared and electrolyzed as above and they behaved in a similar manner to the sodium carbonate solutions. The decomposition potential of the potassium carbonate solutions in respect to the evolution of carbon dioxide was found to be 3.5 volts.

Decomposition Potential of Bicarbonate Solutions

Sodium bicarbonate solutions of various concentrations were electrolyzed at room temperature in the apparatus described above. The decomposition potential on bright platinum electrodes was found to be 2.2 volts over a wide range of concentrations. Evolution of carbon dioxide began in mixtures of bicarbonate and carbonate solutions at a voltage of 2.1 to 2.2. The bubbling of air through a $N/10$ sodium bicarbonate solution into barium hydroxide solution gave no appreciable precipitate of barium carbonate. When the same solution was electrolyzed and the evolved oxygen was allowed to carry over the carbon dioxide formed in the electrolysis, a precipitate of barium carbonate was formed when the voltage reached 2.2.

Potassium bicarbonate solutions indicated a decomposition potential at 2.2 volts, when the apparatus described above was used.

Electrode Potentials

The decomposition potential at which carbon dioxide was evolved from sodium bicarbonate solutions was observed to be about 2.2 volts across smooth platinum electrodes, and from sodium carbonate solutions, 3.5 volts. It was thought desirable to measure the single electrode potentials over a considerable range of voltages in the neighborhood of these decomposition potentials in order to compare them with the electrode potentials for solutions of sodium hydroxide over the same range. It is to be noted that the hydrolysis of these salts gives rise to a small concentration of sodium hydroxide in solution, and that consequently the evolution of hydrogen and oxygen occurring simultaneously below, at and above, the decomposition potentials of the bicarbonate and carbonate solutions, would be due to the discharge of H^+ and OH^- ions. Above the decomposition potentials of sodium bicarbonate and sodium carbonate some of the oxygen evolved would be due to the discharge of HCO_3^- and CO_3^{--}.

Smooth platinum electrodes of 1.0 sq. cm. area were cleaned in hot nitric acid, washed in water and ignited. Freshly prepared 2.0 N solutions of sodium hydroxide, sodium bicarbonate and sodium carbonate were used. The electrode potentials were determined by means of a Leeds and Northrup type K potentiometer in conjunction with a calomel electrode, a salt bridge containing the anion under investigation being used. For voltages above the range of the potentiometer a resistance box of 200,000 ohms was inserted across the calomel electrode circuit and the potential across half this resistance read on the potentiometer and multiplied by 2.

The single electrode potentials were determined at regular intervals over the range 1.9 to 4.5 volts, the intervals being determined on a voltmeter always in circuit across the electrodes. The voltmeter readings also served as a rough check on the potentiometer readings, since the sum of the single electrode potentials should approximate that of the voltmeter. Liquid junction potentials were neglected. The current was read on a milliammeter.

Table I contains the results of the observations recorded to the accuracy of reproducibility. No readings were recorded until the current had been flowing for at least 10 min.

TABLE I

CURRENT DENSITY AND SINGLE ELECTRODE POTENTIALS IN THE d.-c. ELECTROLYSIS OF 2 *N* SOLUTIONS OF SODIUM HYDROXIDE, SODIUM CARBONATE AND SODIUM BICARBONATE

Voltmeter reading, volts	NaOH			Na_2CO_3			$NaHCO_3$		
	Milliamps. per cm.²	Cathode volts	Anode volts	Milliamps. per cm.²	Cathode volts	Anode volts	Milliamps. per cm.²	Cathode volts	Anode volts
1.9	7.5	+0.86	−1.03	5.5	+0.76	−1.12	6.0	+0.42	−1.41
2.0	7.5	+0.93	−1.04	6.0	+0.84	−1.17	7.5	+0.50	−1.43
2.2	10.0	+1.05	−1.11	7.5	+0.93	−1.31	7.5	+0.64	−1.50
2.4	12.5	+1.16	−1.17	10.0	+1.01	−1.41	8.0	+0.74	−1.59
2.6	28.0	+1.22	−1.27	14.0	+1.07	−1.52	10.0	+0.85	−1.67
3.0	40.0	+1.30	−1.61	17.0	+1.13	−1.84	12.5	+1.03	−1.89
3.5	75.0	+1.37	−1.97	20.0	+1.31	−2.08	17.5	+1.14	−2 25
4.0	200.0	+1.50	−2.38	42.0	+1.48	−2.52	30.0	+1.26	−2.71
4.5	250.0	+1.66	−2.78	58.0	+1.62	−2.86	45.0	+1.39	−3.20

The evolution of visible gas bubbles on the electrodes was not observed at a voltage less than 1.9 and, as will be seen from the current density-electrode voltage curves, Fig. 2, this is about the lower limit for any significant changes of voltage with current density.

Fig. 1 is a graph of the electrode potentials corresponding to the impressed voltage across the electrodes, as plotted from the data of Table I.

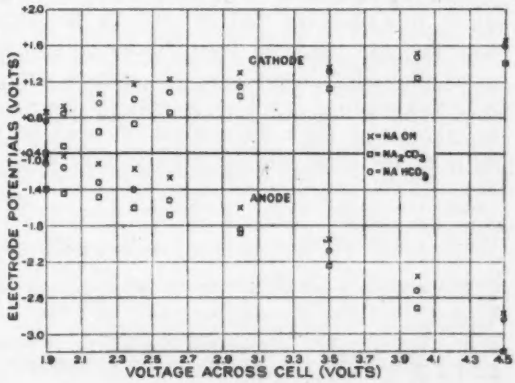

FIG. 1. *Graph showing change of single electrode potential with impressed voltage for sodium hydroxide, sodium carbonate and sodium bicarbonate solutions.*

It will be observed from Fig. 1 that for the same total electrode voltage the cathode potential during electrolysis is always more positive in the sodium hydroxide solution than in the sodium carbonate solution, and even more so than in the solution of sodium bicarbonate. The anode potential on the other

hand is always less negative in the sodium hydroxide solution than in the sodium carbonate solution and considerably less than in the sodium bicarbonate solution. The increase in the potential at each electrode with increase in the impressed voltage is practically the same throughout, although it will be noted that the negative potential increases much more rapidly than does the positive potential. This is no doubt due to the increased polarization of the negative electrode when oxygen is being evolved at increasing current densities as compared with the polarization due to hydrogen at the cathode (1, 2, 3, 4). The effect of carbon dioxide evolution on polarization must be very little, since no marked differences in the relation of the electrode potentials occur at the voltages corresponding to the observed beginning of evolution of this gas (-1.5 to -1.6 volts discharge potential for HCO_3^- and -1.9 to -2.0 volts discharge potential for CO_3^{--}).

The order and magnitude of the differences in potential of the electrodes during electrolysis in the three solutions are in accordance with the (H^+) and (OH^-) concentrations, as would be expected. The sodium hydroxide solution, being more strongly basic than the sodium carbonate, a higher positive potential is required to discharge H^+ and a lower negative potential to discharge OH^- than for either of the salt solutions. Similarly hydrolysis of sodium carbonate produces a higher concentration of OH^- than does the hydrolysis of sodium bicarbonate, and consequently a lower negative potential is required to discharge OH^- and higher positive potential to discharge H^+.

Current Density and Electrode Potential

When the electrode potentials are plotted against current density, as in Fig. 2, it is observed that the cathode potentials for the three solutions do not differ very markedly for the same current density. At current densities higher than 20 milliamp./cm.^{2} the voltage rises more rapidly for the sodium hydroxide solution and least rapidly for the sodium carbonate solution. On the other hand, there is a marked difference in the electrode potentials of the anode at the same current density, that in the sodium hydroxide solution rising abruptly with current densities greater than 10 milliamp./cm.^{2}, as compared with those in the sodium carbonate and sodium bicarbonate solutions. The order of the increasing electrode voltages is the reverse of the OH^- concentration of the electrolyte. At lower current densities there is also a greater spread in the anode potentials as compared to the cathode potentials.

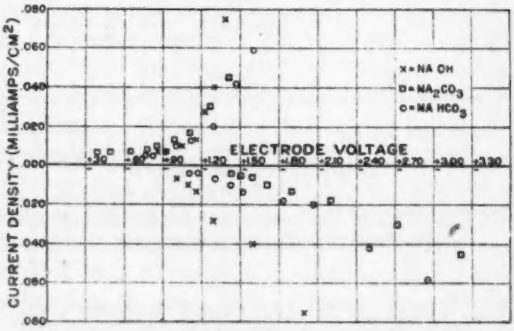

FIG. 2. *Graph showing relation of electrode potentials to increasing current density for sodium hydroxide, sodium carbonate and sodium bicarbonate solutions.*

A relatively greater change in potential with increase in current density takes place at the anode in the neighborhood of the discharge potentials of HCO_3^-, -1.45 to -1.50 volts, and of CO_3^{--}, -1.90 to -1.95 volts, particularly in the case of sodium carbonate. At higher voltages the curves approximate normal decomposition potential curves, that is, the increase in electrode voltage drops off rapidly as compared with the increase in current density.

Discharge Potentials

The discharge potentials of HCO_3^- and CO_3^{--} correspond to the anode voltage at which carbon dioxide was detected in the anode gas discharge, and those of OH^-, to the anode voltage at which oxygen gas first appeared on the electrode. The total electrode voltages corresponding to these potentials were approximately 2.2, 3.5 and 1.9 volts respectively. The electrochemical relations for the discharge potentials may be expressed as in Table II.

TABLE II

Ion	Discharge potential, volts	Electrochemical equation
OH^-	-1.00	$4OH^- - 4e = 2H_2O + O_2$
HCO_3^-	-1.45 to -1.50	$4HCO_3^- - 4e = 2H_2O + 4CO_2 + O_2$
CO_3^{--}	-1.90 to -1.95	$2CO_3^{--} - 2e = 2CO_2 + O_2$

It might be expected that evolution of carbon dioxide would be continuous at all voltages greater than the discharge potential of HCO_3^- even in sodium carbonate solutions, since sodium carbonate produces HCO_3^- by hydrolysis. No such evolution however was observed in sodium carbonate solutions until a decomposition potential of 3.5 volts was reached. On consideration however it is seen that if carbon dioxide were evolved owing to the discharge of HCO_3^- in sodium carbonate solution, it would react with the free alkali formed by hydrolysis to reform sodium carbonate in order to preserve the ionic equilibrium of hydrolysis.

Discussion

No great degree of accuracy can be claimed for the values obtained for the discharge potentials of HCO_3^- and CO_3^{--} ions, because the point of discharge was determined by the appearance of carbon dioxide in the evolved anodic gas. The partial pressure of carbon dioxide from the solutions was an uncontrollable variable affected by the composition of the solution and the temperature. It is to be expected that the decomposition voltages reported will be, if anything, a little high, since the method of detecting this voltage depended on the evolution of carbon dioxide together with that of the oxygen at the anode, and electrolytic decomposition of bicarbonate or carbonate could be recognized only when a distinct precipitate of barium carbonate, which increased visibly on increasing the voltage, was obtained on passing the evolved gas through barium hydroxide solution.

No irregular behavior of the single electrode potentials occurs over the range studied. The effect of the bicarbonate ions, carbonate ions and evolved carbon dioxide on the platinum anode is apparently negligible, as the voltages observed are in conformity with what would be expected from the polarizing effect of oxygen alone and the mutually compensating effect of the H^+ and OH^- ion concentration on the discharge potentials of the cathode and anode.

The inhibiting effect of sodium hydroxide on the evolution of carbon dioxide is probably only apparent and may be explained by the reabsorption of the carbon dioxide by the sodium hydroxide before it reached the barium hydroxide.

Practically, the decomposition potential of water, when platinum electrodes are used, is raised appreciably by the presence of carbonate and bicarbonate, and thus the electrical energy absorption is increased. It would be interesting to determine what this increase actually is in the case of iron and nickel electrodes, and to know whether the sodium hydroxide used technically for the electrolysis of water is sufficiently free from carbonate to obviate any increase in the decomposition potential.

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